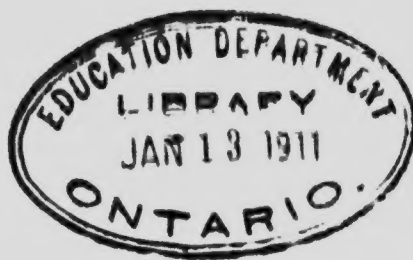# Some Applications of Chemistry to Industrial Processes.

Papers read before the Canadian
Section of the Society of Chemical
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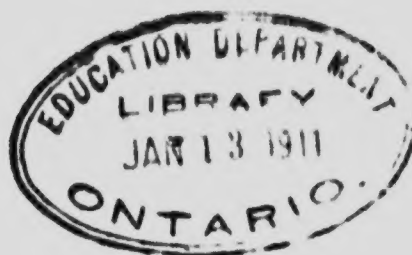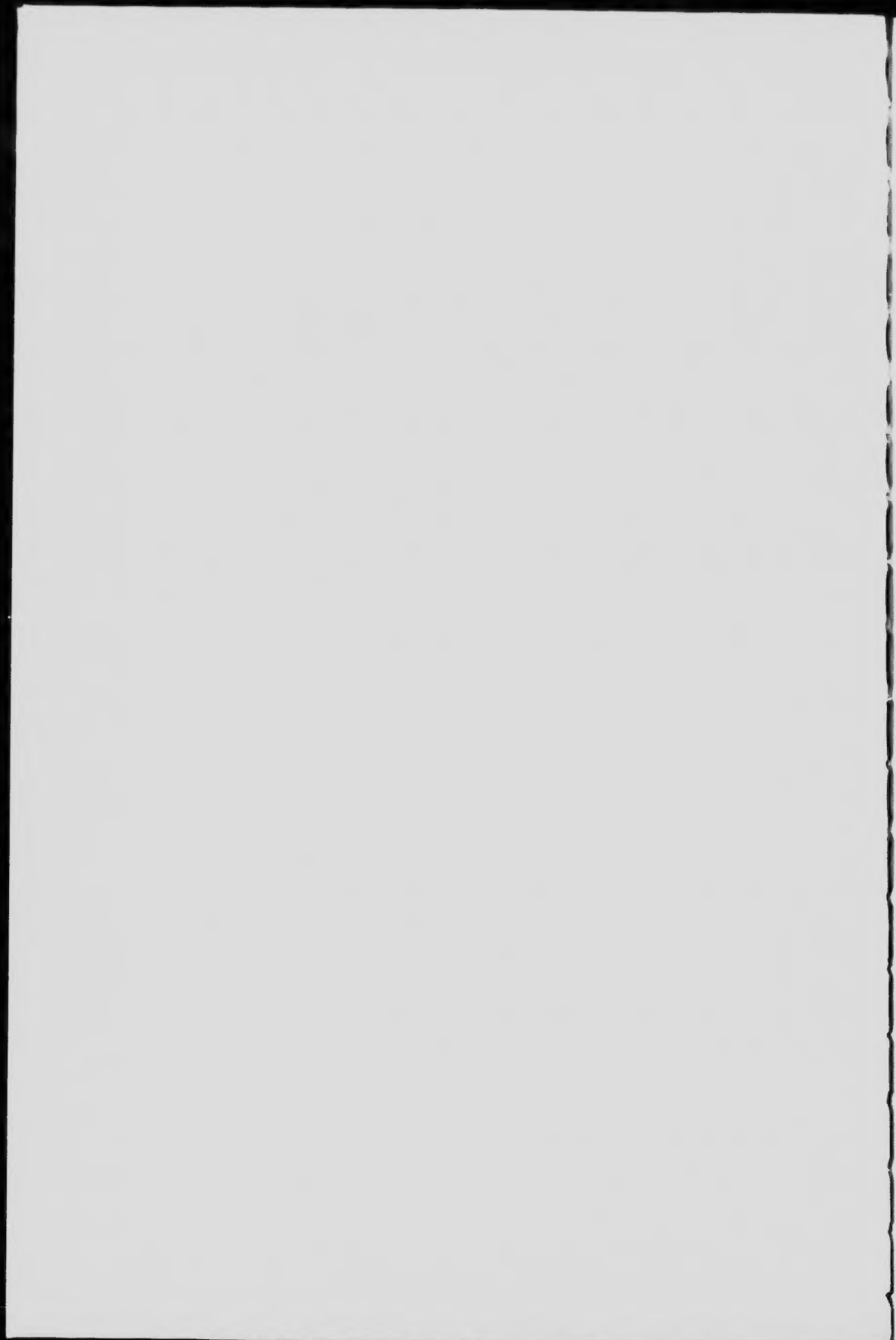|	
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Introduction

The following articles comprise the fourth collection of selected papers read before the Canadian Section of the Society of Chemical Industry and issued in pamphlet form by the committee. The three previous publications dealt with the *Economics of Power Production*, *Some Canadian Industrial Problems*, and *Foods*, and the success which attended their issue has encouraged the committee to print a further volume. The rules of the Society require all papers read before sectional meetings to be submitted to the publication committee in England, but only those which contain the results of original investigation or which deal descriptively with subjects of special interest to members (in that accurate and concise information thereon is not otherwise available) are printed in the *Journal*. The papers and contributions given at the sessional proceedings of a society with so many and varied interests do not always comply with the above conditions; but the Council has recognised their value to members, and has sanctioned the issue by the Canadian Section of such papers as its committee consider sufficiently useful and interesting to warrant their preservation in permanent form. The Ontario Government generously renders financial assistance towards these publications, which are issued to members and others resident throughout the Dominion who are interested in the development of the country's manufactures and natural resources along scientifically economic lines. The contributions now given are by specialists on each subject considered, and the committee hopes that they will receive the appreciation they merit.

The Society of Chemical Industry was founded in England in 1881, receiving a Royal Charter from the Crown in 1907, and numbers at present over 4,200 members. Its chief object is the promotion of those industries in which chemistry plays a part, be it large or small, and consequently manufacturers, engineers and chemists fill its ranks. The *Journal*, which is published fortnightly in London, is the most important periodical on applied chemistry and chemical engineering in the world, and is widely recognized as an invaluable aid to all those whose occupation demands some

chemical knowledge. It is issued fortnightly and contains reports *in extenso* or in abstract form of the papers read before general and sectional meetings, with discussions thereupon: also abstracts of all British, Continental and United States patents on chemical and chemical engineering subjects; classified lists of British applications for patents and "Complete Specifications Accepted"; abstracts of articles relating to applied chemistry selected from British and foreign technical journals and transactions of learned societies; and a classified *Trade Report*, giving information on the Board of Trade returns, statistics, alterations in tariffs, Customs regulations, laws affecting chemical industries, consular reports, new openings for trade and new books. The following divisions, under which the abstracts are arranged, serve to show what industries are represented in the Society:

1. General Plant; Machinery.
2a. Fuel; Gas; Mineral Oils and Waxes.
2b. Destructive Distillation; Heating; Lighting.
3. Tar and Tar Products.
4. Colouring Matters and Dyes.
5. Fibres; Textiles; Cellulose; Paper.
6. Bleaching; Dyeing; Printing; Finishing.
7. Acids; Alkalis; Salts; Non-metallic Elements.
8. Glass; Ceramics.
9. Building Materials.
10. Metals; Metallurgy, including Electro-metallurgy.
11. Electro-Chemistry.
12. Fats; Oils; Waxes.
13. Paints; Pigments; Varnishes; Resins.
14. India-Rubber; Gutta-percha.
15. Leather; Bone; Horn; Glue.
16. Soils; Fertilizers.
17. Sugars; Starches; Gums.
18. Fermentation Industries.
19a. Foods.
19b. Water Purification; Sanitation.
20. Organic Products; Medicinal Substances; Essential Oils.
21. Photographic Materials and Processes.
22. Explosives; Matches.
23. Analytical Processes.
24. Miscellaneous Abstracts.

The Society of Chemical Industry is interested in almost every branch of manufacturing. It is a matter of every-day remark that chemistry is becoming more and more important in the industrial world, and this Society endeavours to furnish a common meeting ground for the manufacturer, the engineer and the chemist. Many of the papers which appear in its journal are quite readily followed and understood by those who have had no technical training, and no progressive Canadian who is interested in industrial affairs should lose an opportunity of keeping in touch with progress abroad as well as at home.

The Canadian Section extends to all who may be interested an invitation to be present at its meetings, the dates of which may be obtained from the Secretary.

Toronto, December, 1910.

THE ALKALOIDS.

By Prof. C. F. Heebner, Phm. B.

Dean of the Ontario College of Pharmacy.

The term alkaloid is applied to a number of physiologically active principles occuring in the vegetable kingdom, and this common occurence is emphasized more than any general chemical character. Like the alkalies, they combine with acids to form salts, and their solutions restore the blue color to reddened litmus, hence the name, alkaloid.

Some of these potent principles are the most valuable of medicines, and others the most dangerous of poisons.

They are found in considerable variety, though a single species of plant seldom produces more than one or a few different kinds, and some plants do not seem to possess them at all. So far, very few alkaloids have been found in monocotyledonous plants, in fact only two that are of importance, viz., colchicine from the corn of the Colchicum autumnale (Meadow Saffron), and Veratrine from the seeds of Cevadilla, while the great majority of the alkaloids are found in the plants of the dicotyledonous series, and, strange to relate, two of the most important families of this group, the two which contain the largest number of species, namely, the natural orders Compositæ and Labiatæ, contain no alkaloids at all.

On the other hand, in some plant families such as the Solanaceæ and Papavereæ, almost every species contains alkaloids. It has not been ascertained that alkaloids are of any service to the plant, except as a means of defence against predatory animals and parasitic fungi. They may even be injurious to the plants which produce them. The poppy, for example, may be poisoned by its own alkaloid, morphine.

It is, perhaps, for this reason that they are not commonly found in large quantities in those parts of the plant where the vitality is greatest, but are accumulated in the less actively growing parts of the bark, in seeds and in fruits —parts sooner or later to become detached from the plant and are thus gradually gotten rid of.

Alkaloids are undoubtedly the products of destructive meta-
bolism, purely waste products, in so far, at least, as nutritive
purposes are concerned; they may, however, as has already been
suggested, be of some use in affording protection against animal
and destructive fungi.

While in a general way the products of destructive change
resemble each other in different plants, in fact, in many cases are
identical, this is not always the case. There are numerous
instances where a compound is produced by a single species or
genus, and is not found elsewhere. The valuable alkaloid, quinine,
for example, is, so far as we know, confined to the genus
Strychnos; the very poisonous glucoside, digitoxin, has never
been met with in any plant except the Foxglove, and the bitter
principle, aloin, is found only in the genus aloe.

Moreover, certain species under certain conditions develop
products which under different conditions are never produced.
This fact is also illustrated in the Cinchonas. When cultivated in
European greenhouses these plants produce no quinine, nor do
they when grown in either too high or too low elevations in their
own native Andes; while, on the other hand, it has been found
that by a proper system of cultivation in a highly favorable
climate, such as the Neilgherry Hills of India, they may be made
to yield three or four times the quantity of alkaloid found when
growing in the wild state, even in those portions of the Andes
most favorable to the growth of these trees.

It is well known also that the potato tuber, when left to grow
exposed to the full sunlight, develops a poisonous principle,
solanine, which, when the tuber is grown normally under ground
it does not possess.

The attraction which the vegetable alkaloids have always
possessed for the chemist, is not in the least surprising; com-
prising, as they do, so small a portion of the composition of the
plants producing them; and yet, in many cases, being responsible
for the entire physiological action of such plants upon the animal
body, it is only natural that their composition should have been
very carefully studied, with a view to an explanation of the
changes by which they are produced in the plants, and, if possible,
to imitate such changes, in order to produce these valuable
remedies synthetically.

In this study, however, chemists found themselves confronted by difficulties of no insignificant character, for even in the determination of the ultimate composition of these alkaloids, their high molecular weights and comparatively small proportions of hydrogen make the exact determination of this element a matter of great difficulty, so that the composition of some of the less known alkaloids has not been definitely established.

It has been known for a long time that the alkaloids were nitrogenous bodies, and they were classed as derived ammonias owing to their manner of forming salts, but for some time nothing more definite could be said concerning their chemical nature.

It is now recognized that the great majority of the alkaloids are derivatives of the basic compounds, pyridine (C_5H_5N) and quinoline (C_9H_7N), but that there are also methane derivatives among them, as caffeine (trimethylxanthine, $C_5H(CH_3)_3N_4O_2$) and theobromine which may be regarded as derivatives of purine, $C_5H_4N_4$, obtained from uric acid, a white crystalline substance melting at 216° C, easily soluble in water, and having the properties of a weak base. Besides the occurrence of these important bases in the plant kingdom, substances answering to many of the alkaloidal tests are produced in the decay of animal tissues, giving rise to the so-called "cadaveric alkaloids" or ptomaines.

It remains true of all classes, however, that we have to do with derived ammonias, either amines or amides, and this feature, must be taken to constitute the basis of their claim to the name, alkaloid, whether synthetically formed, or found in the vegetable or animal kingdom.

CLASSIFICATION.

Leaving the animal alkaloids for subsequent consideration, we may divide the vegetable alkaloids into two classes: (*a*) those which are liquid and volatile, and (*b*) those which are solid and non-volatile. While this appears to be simply a physical distinction, yet there is at the same time a corresponding chemical difference, as the liquid alkaloids are few in number, and contain no oxygen in their composition (being made up of carbon, hydrogen, and nitrogen), and may be looked upon as Amines, built upon the general formula RNH_2, while the solid alkaloids are numerous and are oxygenated bases, and may be considered

Amides having the general formula $RCONH_2$, the exceptions being atropine, cocaine and morphine, which do not contain the $RCONH_2$ group.

FORMATION OF SALTS.

The salts of the alkaloids are built on the same plan as the ammonium salts. When a fixed alkali base is brought into contact with an acid (say hydrochloric), the latter is decomposed, hydrogen is split off and combines with the oxygen of the alkali base to form water, while the acid radicle forms a salt of the alkali metal. When, however, Ammonia is acted upon by an acid, the hydrogen of the acid is not displaced, but the entire acid (hydrogen and acid radicle) combines with the ammonia, forming a salt which was formerly named Ammonia Hydrochlorate (but more properly Hydrochloride), because the hydrogen of the acid had not been displaced, but which is to-day known as Ammonium Chloride, on the supposition that Ammonium, NH_4, a hypothetical base is in existence. When an alkaloid, say Morphine, combines with an acid, say Hydrochloric, it behaves like Ammonia, in that the Hydrogen of the acid is not replaced, and the formula of the resulting salt is $C_1 H_{19} NO_3 HCl$ and is named Morphine Hydrochloride, not Chloride.

Among the general properties of the alkaloids we might mention the following, viz., they are all bitter nitrogenous principles, mostly crystallizable solids; when heated carefully above 100 C, they melt without decomposition, but a much higher temperature decomposes them : they are at most only sparingly soluble in water, but are quite soluble in alcohol and the solvents that are immiscible with water, such as chloroform, petroleum, ether, benzene, amylic alcohol and coal oil; on the other hand, their salts (hydrochlorides, sulphates, nitrates, etc.) are mostly soluble in water or acidulated water, but, with few exceptions, are insoluble in the solvents immiscible with water; they all exert a rotatory action on polarized light, which power is diminished by combination with an acid, though with quinine the reverse is the case.

As to the nomenclature, the termination *ine* (the Latin termination corresponding with this is *ina*) has been made uniform for them as expressing their basic character and their derivation from ammonia. Such terms as " morphia," " quinia," and " strychnia," are therefore obsolete, and are supposed to be quietly relegated to

oblivion, along with the salts of "lime," "potash," "magnesia," etc. The termination *in* (Latin *inum*) is reserved for the neutral principles and glucosides, such as aloin amygdalin, santonin, picrotoxin, glycerin, gelatin, albumin, etc.

Existence of Alkaloids in Plants.

Vegetable alkaloids do not usually exist in the plant in a free state, but generally as a neutral or acid salt of some organic acid, as tannic or malic or lactic, or of some acid peculiar to the particular plant, such as kinic acid in the cinchonas, meconic acid in opium, igasuric acid in nux vomica, etc.

These tannates, meconates, igasurates, etc., are known as the *native salts* when referring to them with methods of extraction, and it is these native salts that are extracted in making the galenical preparations of alkaloidal drugs, such as the solid or liquid extracts, tinctures, elixirs, liniments, etc. While most of these naturally occurring alkaloidal salts are soluble in water, others, such as the tannates, are not, so that for their extraction from the plants either alcohol or acidulated water are used.

For the detection of the alkaloids or their salts in solution, chemicals which form insoluble compounds with them, or which separate the alkaloid in its free state, are made use of. Among these alkaloidal precipitants, we note: (*a*) The alkalies and alkaline salts; these set free the alkaloids, which being insoluble in water, precipitate from aqueous solutions. Such reactions bring about many of the incompatibilities which attend the dispensing of physicians' prescriptions. (*b*) Tannic Acid. The tannates of the alkaloids are quite insoluble in cold water, so that the addition of tannins precipitates them from aqueous solutions of either the free alkaloids or their salts, even when quite dilute. (*c*) The haloid salts of mercury and some other metals, form quite insoluble precipitates with the alkaloids. For instance, bichloride of mercury, or potassium iodohydrargyrate (known as Mayer's reagent) also the corresponding double salts, potassium-bismuth-iodide (Drugendorff's reagent), and potassium-cadmium-iodide (Marme's reagent), gold chloride and platinic chloride precipitate the alkaloids as a double salt, while Lugols' reagent (solution of iodine with potassium iodide) will give insoluble precipitates with the great majority of alkaloids. (*d*) Picric acid (Hager's reagent) precipitates the cinchona bases. (*e*) Phosphomolybdic acid

(Sonnenschein's reagent), and phosphotungstic acid (Scheibler's reagent) are also useful precipitants for the great majority of alkaloids. (/) Potassium chromate precipitates them from the concentrated aqeous solutions of their salts, in the form of difficulty soluble chromates.

The color-tests are at times very strong, but are not generally sufficiently distinctive or exclusive in character to be depended upon for decisive determinations. They are easily interfered with in most cases by the presence of a third substance, and can only be of value when compared with the same test supplied to a sample of the same alkaloid of known purity.

These color-reactions are thus classified by A. H. Allen.

(1) Those produced by dehydrating agents, such as strong sulphuric acid, phosphoric acid and zinc chloride.

(2) Those given by oxidizing agents not of themselves yielding colors, such as nitric acid, chlorine, bromine, and bleaching powder: or sulphuric acid and oxidizing agents, such as potassium chlorate, perchlorate and permanganate.

(3) Those given by oxidizing agents which themselves yield a colored product by reduction, such as iodic acid and reagents containing chromic, molybdic, tungstic, and vanadic acids.

(4) Those obtained by special reagents, such as ferric chloride, hydrochloric acid, sulphuric acid and sugar, etc.

EXTRACTION OF ALKALOIDS.

While the extraction of each alkaloid from its drug means a difference in manipulation according to the peculiarities of the individual alkaloid, a somewhat general idea of extraction can be outlined. In every case, the bark, seeds, leaves, or roots of plants are ground and extracted by infusion, decoction, maceration or percolation with a suitable menstruum. The menstruum, method of extraction, and after-treatment, are largely determined by the nature of the native alkaloid salt.

When the native salt is soluble in water, and the alkaloid itself insoluble, no other menstrum than water is required. An infusion or decoction of the drug is prepared, and the clear extract is made alkaline with sodium or ammonium hydroxide, or milk of lime. The alkali forms a salt with the native acid, and isolates the alkaloid, which, being insoluble in water, precipitates in a more

or less pure form. Considerable judgment must be exercised as to the kind and amount of alkali to be used for the decomposition of the native salt, inasmuch as some of the alkaloids are dissolved by much excess of alkali.

The native salt is often insoluble, or not freely soluble, in water, and in such cases one of the following methods may be followed :

(1) Extraction of the drug by means of water acidulated with sulphuric or hydrochloric acid (which acid forms a water soluble salt of the alkaloid), and then decomposing the clear solution of this salt by adding an alkali to precipitate the alkaloid, which is then collected, washed and dried.

(2) Extraction of the drug with alcohol, and treating the macerate or percolate so obtained with a salt, which, by mutual decomposition with the native salt, yields an insoluble salt of the native acid, and a soluble salt of the alkaloid. Alkali is then added to the filtered solution to precipitate the alkaloid.

Whatever method is used, it may be necessary to purify the recovered alkaloid by redissolving it in hot alcohol, filtering through bone black, and after careful concentration by evaporation, permitting the alkaloid to crystallize, or it may be converted into its sulphate, or other salt, by diffusing it in water acidulated with the desired acid, until dissolved, then evaporating and crystallizing.

In many cases, however, the extraction of the alkaloids involves more complicated processes, in order to remove other plant constituents that are extracted along with the alkaloids.

The free alkaloids differ among each other as to their solubilities in the solvents which are immiscible with water. The salts of the alkaloids (with a few important exceptions), are *insoluble* in the solvents immiscible with water, while certain plant constituents such as fats, resins, waxes, chlorophyll, etc., are soluble in these solvents.

These principles are taken advantage of in the extraction and purification of alkaloids by what is called the " shaking out " process. After obtaining a solution of the free alkaloid in ether, benzene, petroleum ether, chloroform, coal oil, amylic alcohol, or other solvent immiscible with water, it may then be obtained as a solution of a salt of the alkaloid by agitating with acidulated water, then separating and discarding the immiscible solvent which holds in solution many of the valueless plant constituents.

(Demonstration: the separation of quinine from a preparation containing other plant constituents as well, by means of the " shaking out" process).

Qualitative Determination of Alkaloids.

The simplest method for determining the presence of an alkaloid in a drug, is to macerate a small portion of the finely powdered drug in a stoppered flask, for several hours, with frequent agitation, with about ten times its weight of Pollius' Fluid, which is a liquid of remarkable penetrating power composed of, ether, 325 c.c., alcohol, 25 c.c., strong solution of ammonia, 10 c.c. Some of the macerate is decanted from the drug, and shaken in a glass separator with water acidulated with five per cent. of sulphuric acid. Any alkaloid that may be present is dissolved by the acid liquid as an acid-sulphate, and this solution is collected and warmed on a water-bath to evaporate dissolved ether and alcohol. The presence of an alkaloid may then be determined by adding any of the general alkaloidal test-reagents, resulting in the formation of cloudiness or precipitate if alkaloids have been extracted.

Quantitative Determination of Alkaloids. In quantitative estimation, both gravimetric and volumetric methods are used, but the gravimetric is usually preferred, and can be utilized whenever it is possible to isolate the alkaloid in crystalline form, or of any fair degree of purity.

When the alkaloidal residue is accompanied by perceptible amounts of foreign matter, the results obtained by gravimetric methods are too high, and require to be checked by volumetric estimation as follows: The residue should be dissolved, with the aid of heat, in an excess of a volumetric acid-solution, and the excess determined by titrating with volumetric alkali-solution, in the presence of a suitable indicator.

If but one alkaloid be present, this method is most satisfactory, but when several alkaloids are found in the drug, the absence of knowledge as to the relative proportions of these alkaloids, introduces a source of error, which cannot be overcome; in such cases, after purification of the alkaloidal residue by proper means, the gravimetric method is to be preferred for the determination of total alkaloids.

Classification of alkaloids according to their basic compounds.

(a) Pyridine derivatives: Piperidine, Piperine, Coniine, Pilocarpine, Nicotine, Sparteine.

(b) Tropines: Tropine, Atropine, Scopolamine, Hyoscine, Hyoscyamine, Cocaine.

(c) Quinolines : Quinine, Quinidine, Cinchonine, Cinchonidine, Strychnine, Veratrine.

(d) Isoquinolines : Isoquinoline, Hydrastine.

(e) Phenanthrenes : Morphine, Apomorphine, Codeine.

Unallotted: Physostigmine, Pelletierine, Colchicine, Aconitine, Cornutine.

The other alkaloids, such as emetine, gelsemine, cissampeline, etc., are but little understood.

Synthesis of the Alkaloids. Nothing of importance has been evolved through the efforts of chemists towards the preparation of the alkaloids synthetically, inasmuch as the resulting products have not proven satisfactory from a therapeutical standpoint, and therefore are of no commercial value.

Ladenburg, in 1886, successfully accomplished the synthesis of alpha-propyl-piperidine which is identical in composition with the natural alkaloid coniine, found in the fruit of *conium maculatum.*

Since that time piperine and piperidine have been made artificially but all attempts to synthesize the leading alkaloids, *quini-strychnine, atropine, morphine, codeine, pilocarpine, eserine,* c. have so far met with failure, and while substances have bee obtained by synthesis, that somewhat resemble *cocaine* in chemical composition, yet in therapeutic action they fail to meet all of the requirements, and are therefore simply substitutes for this alkaloid.

NOTE. - The speaker then gave an epitome of the history, collection, and cultivation of the more important alkaloid-bearing drugs, viz., *cinchona remejia, opium, nux vomica, coca, jaborandi, calabar bean* and *belladonna*, and presented specimens of these. He further considered the therapeutical and commercial aspects of the alkaloids obtained from these drugs, and of the basic substance, *caffeine.*

GUAYULE RUBBER.

By H. van der Linde.

Past Vice-Chairman, Canadian Section, Society Chemical Industry.

The Guayule Plant belongs to the order of Compositæ and is a small shrub weighing about two pounds and standing about two feet high when full grown. It has a dwarfed and gnarled appearance and contains an extraordinarily small amount of moisture and indeed might be mistaken for a piece of dead wood during a large portion of the year were it not for the fact that on cutting into it, the bark shows a greenish and somewhat moist section.

The shrub grows on the Northern part of the Central Mexico Plateau in enormous quantities. This region consists of rings of denuded mountains with flat plains at their feet. These plains have the appearance of dried-up lakes and it is on the beaches of these ancient lakes that is to say, on a strip of land running around each ring of mountains somewhat above their base, that the Guayule abounds. The alkali soil is usually a gravelly clay covered with flinty pebbles. The subsoil is a magnesian marl called "Caliche."

The Guayule protects itself against loss of water, through evaporation, by possessing a thick bark, in the cells of which solid rubber is secreted forming a more or less complete coating for the plant.

Among all the sources of rubber the Guayule plant is exceptional in that it yields no milky latex the rubber existing in the solid state partially filling the cells of the bark. Rubber is also contained in other parts of the plant but in smaller quantity, although it is quite abundant in the roots. The average amount of rubber is generally taken as ten per cent. A few years ago when attention was first attracted to this plant through the rising price of rubber, attempts were made to extract the gum by means of solvents. Other attempts were made to destroy the woody and barky matters by chemical means and leave the rubber untouched, but the mechanical process has practically superseded all others.

The extent of the industry to-day may be judged from the fact that in 1910 Guayule rubber will form about twenty per cent. of the world's production of all kinds. It is not likely that this rate of production can be kept up, but there is no doubt that ordinary re-growth of the shrub will allow of a large production for many years to come.

The plant is pulled from the soil, baled and shipped by railroad to the factory. Here the process in principle is very simple, but the technical details have presented many difficulties. The plant is crushed to a very fine state of division in the presence of water, the small grains of rubber adhering to one another forming minute worms which are capable of floating while the woody and barky matters sink. The rubber is skimmed off and is packed or baled for market. Special brands are also prepared for specific purposes. These brands are usually more or less deresinated. The resin ranges from 19 to 21 per cent. of the crude dry rubber. It appears probable that the resin acts to some degree as a preservative in vulcanized rubber goods. For some purposes from one-quarter to three-quarters, or even all the resin is extracted, although many manufacturers believe that this process does not influence the quality of the product. Guayule is undoubtedly a true rubber and is almost paradoxical in its nature from the fact that the process of vulcanizing enhances its quality to an extent which brings it into direct competition with other rubbers which sell for higher prices. In rubber goods when properly vulcanized Guayule does not readily deteriorate, its resistance to cracking, etc., being as great as rubbers of a very high grade.

THE DEMANDS OF COLOR FASTNESS ON COTTON.

No Absolutely Fast Color. Fastness an Indefinite Term. Bleeding. Fastness to Rubbing and Perspiration. Fastness to Bleaching, Alkalies and Acids.

By Alfred Burton.

Hon. Secretary, Canadian Section, Society of Chemical Industry.

The fastness of colors is dependent upon certain destructive actions arising from causes which exert themselves in different manners. An absolutely fast color does not exist, so that the term "fast" is only to be used in a comparatively limited sense in regard to the degree with which the colors withstand these influences. We speak of fastness to light and atmosphere, to washing and milling, to rubbing and perspiration, to bleaching, to acids and to the alkalies. The dyer should be certain which of these tests are required of him before the selection of a dye, nay, should demand this information, else his reputation falls shattered to the ground and he is condemned in the eye of the public, and then we are told fast colors can not be dyed at home. Let the ambition of a colorist be a reputation for quality, cheapness should be relegated to the man who goes for quantity only.

The production of uniform goods which have to withstand the action of light, air, and oftentimes rain, for the most part of a day, demand a different test for fastness than, say, an expensive silk which perhaps is never exposed to the rays of the sun, but only shows forth its beauty under the benign influences of artificial light, and perhaps is worn very seldom. In the production of carpets and curtains the fastness to light must be the leading test, whilst for knitted goods the choice of a color should depend upon its fastness to washing.

The researches of Chevreul have proven that even the same dyestuff has not the same fastness on all fibers. For instance indigo extract is the fastest when dyed on silk and the most fugitive on cotton. Vat indigo blue is the fastest on wool and the least so on silk, whilst madder is the fastest on cotton. Therefore,

because a dye is fast on any one fiber it is no criterion that it will be equally so on another. It is also phenomenal that saturated dark shades are faster towards light than the same dyestuff dyed in lighter or unsaturated tones. For example, take the superior alizarin colors which have proven to be the most unsuitable for fast light-mode shades. It is also known that some dyestuffs, such as alizarin, madder and cochineal give with all mordants fast colors, whereas young fustic produces with all mordants unstable colors, whilst logwood will give fast colors with some mordants and fugitive ones with others.

With regard to the artificial dyestuffs they may be arranged in groups conforming to their chemical constitution, and one may safely be sure that in accordance with the arrangement of the atoms within the molecule these groups will be productive of fast or loose colors, showing that chemical constitution seems to play a large part in determining the value of a dye, and most dyestuffs produced from a base such as anilin are mostly fugitive, whereas alizarin and its derivatines are mostly fast.

United Action of Light and Atmosphere.

The united action of light and atmosphere subdue every color, though some few only after a long lapse of time, noticeable by the gradual fading of the color. Indigo, world famed for fastness, gradually darkens during the first year, then gradually fades away, and it seems a truism that as the sun gives us our beauteous colors, so does it take them away. The dyer possesses no means of strengthening the fastness to light and air, except in the case of a few isolated colors, and yet the color must be more or less fast, especially in such goods as hosiery, underwear, corset covering, linings, etc., and in a much stronger degree in dress goods, awnings, etc. The only way of escape is the proper choice of the dyestuff, and to achieve this end the dyer must have recourse to an exposure test, made somewhat after the following manner :

A dyed sample is half covered with a thick removable paper covering and exposed to the light in the open air, being hung up in a locality where it shall receive the rays of the sun, but at the same time be protected from the weather. At specified times the paper covering is gradually pulled over the exposed portion, say half an inch at a time, until the last half inch is reached, when the gradual fading of the color may be seen at a glance by the removal

of the covering and the time noted. For a standard the result
may be compared with a sample dyed with indigo blue or turkey
red. The samples are observed daily and the day noted when the
first change in color is noticeable. In summer it takes usually
12 to 15 days for indigo blue, and 25 to 30 for turkey red ; in
winter about double this time is necessary. Considerable practice
is required in noting the first change which takes place in the color,
and it is only after repeated trials that one becomes expert in dis-
tinguishing the characteristic changes which take place with the
different colors. Thus the fading indigo blue retains its original
dull tone, whereas the bright methylene blue becomes duller than
paler. The fading action is, therefore more discernible in the
latter than in the former, and readily gives one the opinion that
indigo blue is faster to light than methylene blue.

FASTNESS TO WASHING.

Probably the most important, at all events of paramount im-
portance, is fastness to washing. How often is a muslin or
gingham condemned after it has made its reappearance from the
laundry? No longer to be recognized as it once was, the joy of
its wearer, though the salesman assured the fair purchaser that it
would wash. To meet this requirement the color must withstand
both a mechanical friction as well as the action of an alkaline solution
under various high temperatures. Under these conditions the
color may not even change its tone, but may bleed and stain other
colors woven or printed alongside, especially in the case of white.
Such a color alongside would not be considered fast to washing.

Absolute fastness is only shown approximately by a few dye-
stuffs, such for example, as aniline black by the oxidation process.
Any deleterious action in washing is due to the free alkali in the
soaps used. Neutral soaps, even the ordinary tallow soap itself,
are not generally of much danger, but often the common household
laundry soap is a yellow variety (itself a fast color) containing in a
large measure free alkali. Ultimately the last portions of the
mordant are destroyed, which is the means of binding together
fiber and color, thus freeing the fiber of its color. Therefore
stronger mordants should be used so that the free alkali present
shall have a superfluity of mordant to counteract it, and also such
dyestuffs should be chosen, the lakes of which have a greater
resistance towards alkalies, as New Blue (Cassella), Indophenin
(Baeyer), Catechu, etc.

BLEEDING.

The bleeding of self-dyed goods, even if the color is not changed, may not be harmful nor displeasing, but it is especially detrimental on mixed fabrics or those containing white. In this case, the active destructive principle is the temperature of the wash-waters. For instance, colors dyed with saffranine will turn bluer and bleed into white in distilled water at 75 degrees C., and still more decidedly at the same temperature in a weak soap solution ; but the same color in a much stronger soap solution will not bleed in a temperature of only 30 degrees C. In a similar manner many other coal-tar dyes are affected. It goes, therefore, without saying, that the bleeding in most cases may be prevented by using a wash-water not warmer than 30-35 degrees C. As a matter of fact, household washing of colored goods is done at a much lower temperature than white goods ; and so unreliable is guessing at the proper temperature without the use of a thermometer that too great emphasis can not be laid upon the advisability of casting aside such dyestuffs for use in dyeing vari-colored effects, whose lakes bleed easily under these conditions.

Natural and mineral dyes never bleed, also several aniline dyes, especially when dyed in full tones. Decidedly unacceptable in this case are most benzidine dyes with the exception of the diazotised diamine colors. Most benzidine dyes bleed even in light shades, in weak alkaline solutions only slightly warmed, and repeated washing in water does not seem to eradicate this fault. White and other colors woven together take up speedily the color as it bleeds off. However, benzidine dyes show a characteristic fastness in another direction possessed by no other dyes, turkey red not excepted, in that after repeated washing and bleeding the brightness and depth of the shades seem hardly to be impaired. For self-colored wash-goods these dyes are very advantageous, also for fancy goods where the other dyed fiber is wool, as by severe washing the wool does not take up the color that bleeds off the cotton.

RUBBING AND PERSPIRATION.

As regards fastness to fulling, an article such as this would be of very little moment as the cotton fiber does not lend itself to this process and would only be required to resist this influence where it is used as an effect thread in woolen goods. Therefore we will pass over to the more important demands of the trade—fastness

against rubbing and perspiration. This requirement is of utmost importance in the production of hosiery and knit-goods, yarns, and corset coverings and linings, and should be taken seriously into account for goods used by the making-up trade in the manufacture of under-skirts. The color should not rub off nor soil light-colored or white underwear, nor come off on the hands or gloves of the wearer. As a remedy, precautionary methods are taken partly by means of the addition of a sizing material to the dye-bath or printing paste which is dried upon the fiber and in a mechanical manner causes any loose color to adhere to the fabric, in part by a final passage through a tannin bath, whereby the dye forming the color lake in the under layers of the fiber is fixed in a chemical manner, and also by soaping the goods after washing, and in this way removing any loose or uncombined dye from the face of the material. Still any or all of these operations do not always give satisfactory results; the color will rub in spite of all, the color-lake has not penetrated the fiber sufficiently deep and has only fixed itself mostly upon the surface. The cause of the rubbing, therefore, is not on account of the dyeing process, but in the behaviour of the dyestuff to the fiber.

Cotton possesses divers attractions for the absorption of lakes, and only such dyes for which the fiber has an attraction will produce results fast enough for rubbing. Indigo, for instance, which is squeezed from the fiber, and on that account always rubs, is exactly different from the benzidines which will not rub of themselves. Further such colors as methyl violet, magenta, and saffranin, rub badly, whereas Saffranin S, Methylene Blue, Methylene Violet (Hoechst), New Blue (Cassella), Indophenin (Baeyer), and such like are satisfactory towards rubbing. The proof consists in rubbing with the hand on white paper not too smooth, or better still, with an unsized cotton rag.

Fastness to perspiration is often demanded besides fastness to rubbing, more especially with goods that come in contact with the skin and absorb, or take up, the secretions thereof. Perspiration is composed almost wholly of water and traces of several acids, such as butyric, acetic, and formic, and also phosphoric acid salts. The action of these bodies is exerted through the influence of the heat of the body and friction, and above all none the less aggravated by the concentration on the fiber of the perspiration with all its ingredients, through the continual drying out of the perspiration,

which in time becomes even detrimental to the fiber itself. The best test is to wear under the arm or sole of the foot, the sample to be tried, or, for a laboratory trial make a weak acetic bath with distilled water and acetic acid of 30 per cent., heat to about 37 degrees C., the approximate temperature of the body, dip the sample therein and rub it with the hands for a minute or two, then, without washing, allow to dry at the ordinary temperature, and also between two pieces of parchment at 25 to 30 degrees C. This is repeated several times, and the more often it is done the nearer to nature does it come.

BLEACHING.

Another requisite demand for color fastness in cotton goods is towards chlorine or bleaching. This is necessary where the goods are to be bleached after dyeing for the purpose of bringing out undyed parts of the fabric in a cleaner white. The operations, as are well known, are boiling under pressure, after treatment with chloride of lime, muriatic acid and soap. The boiling in water for such colors as are not destroyed in hot water, or for which the fiber has more or less attraction is not detrimental, in fact, is rather advantageous, because the steaming tends to complete the combination between fiber and color.

Chloride of lime is very energetic in its destructive action on both natural and artificial dyestuffs alike, while dilute muriatic acid is of very little account in attacking colors which are fast to chemicking. It, on the contrary, is more energetic in its action on colors destroyed by bleaching, causing them to entirely disappear. The only influence of soap is, practically, in rendering the fiber more pliant and agreeable in handling. Colors fast to chloring are the colors produced by the oxide of iron, red liquor, and the like, in combination with alizarin.

To test colors for their fastness towards bleaching, it is best to boil first, as many vat blues and turkey reds are topped with direct dyes. If bleeding takes place it proves the presence of benzidine dyes. Afterwards place the sample to be tested in a cold, clear solution of chloride of lime, about two degrees Beaumé, for 1 to 1½ hours, wash well and pass through a weak sour, wash again and dry. Any color standing this treatment may safely be used for fancy woven effects which require bleaching afterwards.

The fastness to acids and sulphuring is, also, like fastness to milling, rarely demanded of the cotton goods dyer. It is more essential when turkey red or indigo blue is used for a fine cotton thread effect in all-wool goods with cream or white grounds that require a final sulphur bleach. So the general cotton dyer need not apply himself to this, unless he is producing goods afterwards to be handled by the rubber manufacturer.

SELECTION OF DYES.

It goes, therefore, without saying that the selection of dyes is of the utmost importance, and that too much time and attention can not be bestowed upon such an important choice. As a basis for a comprehensive plan to meet the demands of most cases the following tables will be found useful. It is known that fastness to washing is seldom found in combination with equal fastness to light and rubbing, so that the most important points should be taken into account first.

1. The demand of color fastness for hosiery and knit goods : (*a*) fastness to rubbing ; (*b*) fastness to washing ; (*c*) fastness to light.

2. The demands for yarns for wash goods : (*a*) fastness to washing ; (*b*) fastness to light ; (*c*) fastness to rubbing.

3. The demands for yarns for wearing apparel not requiring to be washed : (*a*) fastness to light; (*b*) fastness to rubbing; (*c*) fastness to washing (in so far as to withstand the finishing process).

4. The demands for curtains, covers, carpets, fringes, etc. ; (*a*) fastness to light ; (*b*) fastness to rubbing.

MAIZE PRODUCTS, AND MAIZE STARCH AND ITS PRODUCTS.

By W. P. Kaufmann, M.D., C.M.

In the manufacture of starch from maize, the dry grain is first steeped for from two to four days in warm water containing sulphur dioxide. The steeped grain is next run through mills where it is cracked, decorticated, and partially ground, giving rise to a semi-liquid mass. This so-called "separator liquor" is then passed through a germ separator; the germ is skimmed off by paddles, it is washed as free as possible from adherent starch, dried, "cooked" with live steam, and its oil expressed in hydraulic presses. The resulting corn oil is used largely in the manufacture of soap, and the oil cake, which is rich in protein and fat, as a cattle feed (analysis given).

The endosperm, starchy and glutinous matter, cortical tissues, bran and fibre which compose the "separator liquor" are next screened, the coarse material ground in burr-stone mills and returned to the "separator liquor" which is fed to shakers of silk bolting cloth. The branny portions of the grain are caught, washed as free from starch as possible, squeezed in presses to remove water, and sold as press feed for cattle.

The liquors from the shakers, known as "mill liquor" or "crude starch liquor," are screened a second time and then passed over the "runs," "tables," "trays" or "gutters," these terms being used synonymously. In the "runs," which have a drop of four inches in one hundred and twenty feet, the starch is deposited. The tailings, concentrated in settling tanks, may be sold as "slop" or "swill," or pumped through filter presses, dried and sold as gluten meal which analysis shews to be high in protein. Mr. F. T. Shutt of the Central Experimental Farm, Ottawa, considers that maize protein is the most efficient source of nitrogenous food for cattle, swine, etc.

The "green starch" deposited on the "runs" is shovelled off, stirred up with water in the "breaker," and either "converted"

into glucose or grape sugar, or manufactured into the different varieties of starch to meet the various industrial and domestic requirements.

The maize starch sold on the Canadian market may be classified as "unchemicalled" and "chemicalled." "Unchemicalled" starch is used in the manufacture of baking powder, in the textile industries, and to a small extent by steam laundries. The "chemicalled" starch has been treated with alkali to cause swelling and flocculation of the protein and fibrous matter and saponification of the fat, inducing these to "tail off" and leave a purer and whiter starch. The laundryman and the confectioner consume the bulk of the "chemicalled" starch. Their requirements are such as to necessitate not only very uniform grades of starch but certain other characteristics which open up the whole question of the manufacture of "thick-boiling" and "thin-boiling" starches; this question is too voluminous to be properly handled in an abstract, and the reader is referred to the original.

CUSTOMS CHEMISTRY.

By F. W. Babington.

Chemist to H.M's. Customs, Ottawa.

Many well considered chemical industries have failed in the Colonies from a want of knowledge of the operation of the Customs Tariff on imports and the Excise taxes on manufactures.

No Customs Tariff is scientifically drafted. It is drafted from a commercial standpoint, and its phrases and definitions are entirely commercial. If scientific standards and definitions were embodied in it, it would lead to injustice, so they are eliminated as much as possible. The onus of proof is naturally on the importer; if he imagines he is discriminated against, he protests; his arguments must be good from a commercial point of view; chemical arguments should be eliminated, as they are useless. An example will suffice. Oil of vitriol (sulphuric acid) was claimed to be a chemical compound, as consisting of sulphur, hydrogen, and oxygen. The answer was, that admitting this, so was water. The same answer was given in the case of a claim that common salt and sodium chloride were one and the same.

The Customs Tariff is as much a judiciary act as a statutory law. The officials have only administrative powers; they cannot change the Act by "jot or tittle". They can and do give relief in certain cases where injustice is manifest, but these relaxations are " without prejudice " and can be rescinded. It takes an Order in Council to change a clause or modify it; it would take a division of the House of Parliament to change the Act.

A chemical manufacturer, intending to establish an industry in Canada, would naturally apply to the Department for the rate of duty on his raw material. He would receive a carefully worded reply that the duty on such goods would be so much, but that the Department would not bind themselves until the goods were actually imported. Very prudent of the Department; for often, from ignorance, other but similar goods are entered, and a different rate of duty charged. For example; he enquires for the duty on sulphites, meaning sodium bi-sulphite, and is answered that it is free under item 210 T. He imports hyposulphite or calcium

bi-sulphite and finds that it is dutiable and alleges a breach of faith. There is no similitude clause, properly speaking, in the Tariff; the goods must be specified, or else they are "unenumerated."

An importer enters dried soda alum, and employs a Customs broker to pass the entry; the broker enquires as to composition; is informed that it is practically sulphate of alumina; enters it under item 212 T. The Appraiser at the port disputes it; the sample is referred to the Department; on analysis practically no water and 20 per cent. Na_2SO_4 are found. The alum is refused entry under 212 T. and a call is made for amended or post entry. All this trouble and delay might have been avoided by a frank declaration at first.

The Government Analyst is simply the chemical adviser of the Department. He has no administrative powers. He reports his opinion to the Appraiser, as a chemist. The Appraiser acts on his advice or submits it the Board of Customs, which meets periodically and discusses questions of rating, and from their decision, their is only an appeal to the Minister of Customs.

The Laboratory work is necessarily sketchy good qualitative work and as little quantitative as possible. In fact, quantitative estimations are only made when necessary to ground an opinion on figures or are called for by the Tariff. The reason is evident. The analyst has a large range, reporting on everything from tin tacks to smokeless powder, and his average of samples is 10 *per diem*, besides a large amount of clerical work by the assistants, and any delay on his part holds up the importation; consequently rapid and fairly accurate results are sought for; but where the Tariff calls for quantitative results, the goods are carefully tested. This is not so onerous as it appears, as the bulk of samples have been previously analyzed and it is a question of confirmation.

There are many Excise and Customs chemical problems which are not understood by the average Analyst. A few may be cited, viz.:

Alcoholic Determinations. The Customs and Excise express and tax alcohol in terms of proof spirit. Proof spirit in Great Britain is: "a dilute spirit of which 13 volumes shall weigh the same as 12 volumes of water at the same temperature," Sp. Gr. of .91984 at 60 Fahr. or Sp. Gr. of .91817 at 62 Fahr. It contains (*vide* Fownes and Hehner) alcohol by weight, 49.24 per cent., by

vol. 57.06 per cent. Taking "proof spirit" as 100, absolute alcohol equals 75¼ over proof or 175.25 proof spirit. Thus 100 volumes absolute alcohol would make 175.25 volumes proof spirit, and the duty at $2.40 per gallon proof would be on that basis, 175.25 × $2.40; taking 20 under proof or 80 per cent. proof spirit, duty is on 80 gallons proof to the 100 entered. Taking 20 over proof or 120 per cent. proof spirit, the duty is on 120 gallons proof to the 100 entered.

Now this arrangement for duty purposes is not so absurd as it appears. It is grounded on weight, whereas the other methods of computing alcohol are grounded on alcohol by volume. The specific gravity of absolute alcohol is open to doubt; it leads to misunderstanding when proof spirit is compared with alcohol from other nations. Continental nations use the Gay Lussac Centismal Alcoholometer, reading absolute alcohol by volume as of a Sp. Gr. of .7947. Since then the Sp. Gr. of alcohol has been found to be .7938 (Keene's Handbook), so the standard is uncertain. That fact is so well known that tables are given in Salleron & Dujardin's *Instruments de precision appliqué à l'oenologue* for converting degrees Gay Lussac into Sykes Hydrometer and Tralles Hydrometer degrees. In the United States Tralles tables are legalized. The alcohol is per cent by volume. Proof Spirit is used by U.S. Excise; it is described as an alcoholic liquor containing one-half its volume of alcohol (Sp. Gr. .7939) giving a Proof Spirit of Sp. Gr. .93353, water at 4 C. being taken at unity.

Therefore British at 60 Fahr. = Sp. Gr. .91984
U.S. at 60 Fahr. = Sp. Gr. .9341

The U.S. Proof Spirit = 42.7 alcohol by weight; British 49.24. So in checking invoices the spirit strengths of the different nations are not comparative, neither is the volume. Continental nations measure in litres; the British imperial gallon is 160 oz., wine gallon, 128 oz. The U.S. standard is wine measure. All this must be taken into account when comparing the declaration on the invoice with the Customs or Excise test.

Spirit Analysis. Unsweetened spirits are tested by Sykes' hydrometer, sweetened spirits and cordials are distilled, and the specific gravity of distillate taken by a pycnometer or specific gravity bottle, and Hehner's tables are used. The hydrometer is accurate for ordinary spirit strengths, but inaccurate when the alcoholic strength is high, *i.e.*, over 80 per cent, or when it is

low, *i.e.*, 20 per cent. proof spirit and under. For high alcohols the specific gravity bottle is used; when it approaches absolute the Westphal or Mohr's balance is more accurate, as it is not affected by expansion.

For low alcohols such as wines, the ordinary Sykes' hydrometer should not be used, as its stem is only divided into $\frac{1}{10}$ and each division is equal to $\frac{1}{10}$ or 6 per cent. proof spirit; so either the specific gravity bottle or the special wine hydrometer is used.

Flame Test. In distillates from liquids, flavours, etc., which contain a very small amount of alcohol, it is sometimes a matter of doubt whether the specific gravity of the distillate really represents the alcohol. It is accordingly re-distilled, only a few c.c. of distillate being collected in a test tube, boiled, ignited by a match. The simple flame test on 50 c.c. of the original heated in small-mouthed flask and the vapour ignited, will show 1 per cent. alcohol or 2 per cent. proof spirit. Volatile oils in alcoholic solution are distilled to mark, shaken with heavy gasoline, separated, specific gravity of aqueous layer taken or the alcohol removed by shaking with saturated salt solution and distilling. For the identification of methyl and ethyl alcohols a few drops are placed on recently ignited platinised asbestos or platinum black; methyl alcohol is oxidised to formaldehyde; and ethyl alcohol to acetaldehyde. Acetone gives no characteristic odour; if acetone is suspected, it is separated by calcium chloride and confirmed by iodoform te .

Vinegar and acetic acid are both rated for duty in terms of acetic anhydride ($C_4H_6O_3$) which has a molecular weight of 102, acetic acid ($C_2H_4O_2$) has a molecular weight of 60, therefore the relation is as 60 : 51, that is the acetic acid found must be multiplied by 0.85.

Example Vinegar containing 7.2 per cent. acetic acid contains 6.12 per cent. acetic anhydride. As the strength of Proof 6 per cent. acetic anhydride, then 100 gallons of the above vinegar would equal $\dfrac{6.12 \times 100}{6}$ 102 Proof Gallons, that is it would be 2 over proof. This leads to some confusion in checking invoices, as the Customs and Excise test appears to show a weaker strength than is indicated on the invoice.

As an example an importer paying duty on a certain importation on the basis of acetic anhydride, found on comparing the

official test with the invoice that there was a considerable difference, the official test being less—he naturally imagined he was defrauded. It was referred to an analyst who certified the invoice was correct as regards percentage of acetic acid. A protest was made, but when the matter was explained and the acetic acid calculated to anhydride, the results were identical.

There is another trouble in interpreting acetic acid. The acetic acid is sometimes designated by a number; this is based on per cent. proof; thus No. 8 acid is that acetic acid which, when diluted to 8 parts, will yield 4 per cent. acid, i.e., proof. Thus No. 8 is 32 per cent. acetic acid, No. 12, 48 per cent. acetic acid. In the trade "Vinegar Numbers" are used that equal the number of grains of dried sodium carbonate neutralized by 1 fluid ounce (Imperial) of the vinegar. The ratio of sodium carbonate to acetic acid is 1 to 1.132, therefore the grains of absolute acid per fluid ounce of 437 grains is obtained by multiplying the number of grains of sodium carbonate required by 1.132 and then by the specific gravity of the vinegar. In the United States the vinegar or acetic acid is reckoned in terms necessary to neutralize 35 grains potassium bicarbonate per oz. Troy—item 288 U.S. Tariff.

These are a few examples of Departmental regulations which might puzzle an analyst. The bulk of the questions are generally on interpretation of results. The analysis is seldom objected to; the opinion is open to discussion. To give the processes used for all and every question that arises, an official Encyclopedia would be needed, as during last month, 172 samples of Sugar, 50 Molasses, and 80 various, or a total of 312 samples, were handled at Ottawa by the Analyst and his staff, consisting of Analyst, Assistant Analyst and two Sugar Observers.

ELECTRO-METALLURGICAL PROCESSES.

By J. C. King.

Electro-metallurgical processes may be said to have originated in their simplest form when Sir Humphrey Davy succeeded during the year 1800 in decomposing some alkaline-earth oxides by the use of a galvanic battery, but, like the first step in many of the discoveries in science, very little real progress was made in the art until towards the end of the century. There are at least three prime causes for its slow development from 1800 to about 1885. *First.* The development of the electric dynamo was not sufficiently advanced to be relied upon to supply the necessary electric current to operate successfully any electro-metallurgical process. *Second.* There were no very large units of mechanical power obtainable at a reasonable outlay. *Third.* There was very little demand until the end of the 19th century for the products of the electric furnace, and whatever demand there might have been, could in most cases be supplied from other sources. It is due very greatly to the progress in the arts of chemical and metallurgical science that these products are required, as the greater number of them are used in the more advanced stages of the various processes in which they enter, and to improve rather than replace other substances. To this demand for better materials and higher efficiency generally the electro-metallurgical process owes its existence. It will therefore be readily understood why the successful dynamo is followed closely by hydro-electric (as well as other power development) and by rapid progress in electro-metallurgical processes.

The Electric Furnace in its various types is the mechanical apparatus in which these processes are carried out.

There are three types of electric furnace now employed, namely: (1) arc, (2) electrolytic, and (3) incandescent (or resistant).

In the construction of these furnaces all conductors in the path of the current are designed to reduce resistance to a minimum, and thereby localize the heat within the zone of reduction in the furnace. The differentiating characteristics of each type of furnace may be briefly outlined as follows:

(1) When the zone is gaseous an arc is formed, extreme temperature being attained, and this arc is the agent by which the electric energy is converted into heat, obtaining the temperatures which are necessary to dissociate combinations of elements as found in nature, and obtain pure metals thereby, or to cause new combinations of elements resulting in new and useful compounds, and in other cases to cause the union of elements which may be associated but not combined (as in the case of nitrogen and oxygen in the air). It should be noted that the arc transformation and application of the electric energy is mainly thermal in its action.

(2) When this zone of reduction contains substances liquifying and boiling at a high temperature, direct current being used, electrolysis usually results, and the liquid condition of the mass assists the electrolytic separation, the metal being deposited on the cathode or negative pole of the furnace or cell used. Here the high temperature of the arc is not required.

(3) When material such as carbon, graphite, carbonaceous mixtures, as well as metals having a high melting point form the zone of reduction, the incandescent or resistant effect is wholly or partly produced. The point of most importance in the incandescent application, although practically the same as the arc in its action in producing a thermal effect also, is that the heat can be regulated much more easily, making it possible to get some results that would not be obtained in the arc, especially in a commercial way. Therefore, in view of these observations, it is advisable to take up the description of electro-metallurgical processes (by which some 20 or more metals and compounds are produced) under the divisions as indicated by those of the electric furnace, and a more detailed description of some of these processes under each head will be dealt with later. It is, however, not intended that these divisions should be adhered to too rigidly, for in almost every application of the electric current to smelting and reduction processes, the effective phenomena are usually not confined to those exhibited in any one of the three types just outlined, but phenomena peculiar to two or even all three types may be invoked.

Now that we may start with a thorough knowledge of the practical operation of one of the simplest of these processes, as far as mechanical apparatus is concerned, a description in detail

of the making of an experimental test will be of assistance. One can get only a small number of practical results when the arc type, strictly speaking, is used to produce a pure metal, as it is almost impossible to obtain anything but a maximum temperature, resulting in volatilization where smelting operations are to be carried on in the arc itself. For experimental work, where the question of efficiency is not always of importance, the arc is very suitable, and especially so where alloys and refractory compounds are to be produced. The furnace is simple and inexpensive, requiring little room or apparatus, and high temperatures are attainable almost instantly, making it possible to conduct experiments that with the other types of furnaces are impossible. Small charges may be treated without much delay, and, consequently, many trials can be made in a comparatively short time. The product it is desired to obtain will frequently, however, not stand the temperature of the arc, since volatilization results, and the product is driven off and generally recombined with other elements, usually oxygen from the air or from the charge being treated. This may be partially overcome by keeping the charge a little way from the high temperature zone.

The experimental electric furnace is a very simple piece of apparatus, the crucible, of graphite or carbon, is placed on an iron plate which is in electric contact with one pole of the dynamo. Suspended directly over this crucible is a carbon or graphite electrode about 4 ins. in diameter clamped or screwed into a holder to which the other pole of the dynamo is connected. This electrode can be moved up and down by a gear, the shaft of which extends out to a hand wheel. For the successful operation of this furnace it is desirable to have about 20 to 30 kilowatts delivered at about 50 volts. Let it be supposed that a test is being made to produce ferro-silicon: an intimate mixture of approximately 35 lbs. of quartz, 15 lbs. of iron ore, 20 lbs. of carbon in the form of coke is prepared, the current is thrown on to the furnace circuit, and the hand wheel is rotated so as to bring the electrode into contact with the bottom of the crucible to form an arc, the electrode is then drawn away from the bottom sufficiently to give the required current, and the quartz, iron ore and coke mixture is fed in slowly until the arc is completely covered. The feeding in of the mixture and regulating the electrodes is carried on from time to time as required, and metal can be tapped if it is desirable

to do so, but usually in experimental work the charge is allowed
to cool after an hour or two's run and is then dumped out for
examination and analysis, which should shew about 50 per cent.
silicon and 50 per cent. iron.

This process seems remarkably simple, and in many ways it is,
the reaction which takes place being represented by the formula
$SiO_2 + 2C = Si + 2CO$, not considering the iron oxide. The experi-
ence of the manufacturers working on a commercial scale, how-
ever, is that it is a difficult reduction process, since the quartz or
silica, when in a liquid state, forms in the furnace a very tough
sticky mass which renders the silicon difficult to collect. The
presence of the iron, however, helps in this direction by increasing
the specific gravity, and thus carrying the silicon to the bottom of
the furnace from which it can be tapped. Great care is required
to prevent the furnace becoming clogged up with a slaggy mass
of fused silicon which would necessitate rebuilding the furnace.
In the production of ferro-silicon a uniform analysis is desired,
this adds other difficulties, which necessitate very careful furnace
operation and attention to the raw material entering the furnace.
Theoretically 60 lbs. of silica and 24 lbs. of carbon are required to
produce 28 lbs. of silicon, but in practice different proportions are
used on account of losses. One kilowatt-day of electric current is
required to produce 5 to 6 lbs. 50 per cent. ferro-silicon.

This description of an experiment in a laboratory furnace will
give a fairly clear idea of the manner in which some of the most
extensive present-day electro-metallurgical processes are carried
out. The chief differences between the small experimental ap-
paratus and the commercial plant are duplication, and design of
furnaces and apparatus to accomplish the desired results with the
greatest possible economy in electric energy. There have been
many designs of furnaces proposed, but a description of the
fundamental types necessary to properly explain the particular
processes selected as typical will be all that is necessary. It would
not be practicable to describe all the experiments and the most
recent changes that may have been made, or are under way in
many operations. These changes have resulted in large savings
in power, raw materials and labor. We shall now take up in
more or less detail one or more processes under the divisions
previously mentioned.

The first which comes to our attention is distinctly an arc
process, known as the "Birkeland-Eyde" for the fixation of

atmospheric nitrogen, producing nitric acid. The formation of nitric oxide by the arc was observed by Priestley and Cavendish in the year 1775, but no practical use was made of the knowledge until recently.

During the past 6 or 8 years, and up to the present time C. Birkeland and S. Eyde have been the most successful in the production of nitric acid by the electric process, although only about 2 per cent. of the air passed through the furnace is said to be oxidized.

The furnace or oven is designed to take advantage of the well-known fact that a magnet will deflect an arc at right angles to the lines of force in its field. When the deflection becomes great enough the arc breaks, when another straight one will be instantly formed, the arcing, deflecting and breaking going on as long as the current is supplied, the rates of interruption in the operation of this process being several hundred per second, although many more interruptions may be caused to take place. The reason for deflecting, and finally breaking this arc, being to thereby produce an arc of the flaming type which makes it possible to bring a greater quantity of air in contact with it for conversion. A direct current produces an arc having the appearance of a semi-circular disk, an alternating current deflects the arc by causing the striking points to move backward from the ends of the electrodes.

To operate the Birkeland and Eyde furnace a current of 5000 volts is used. A furnace of 500 kilowatts capacity gives better results than one of 200 kilowatts which was the capacity of the furnace formerly used, the former giving 900 kilograms per kilowatt-year, while the latter or small one only gave 400 kilograms per kilowatt-year.

To start the furnace, alternating current (as now used) is turned on to form the arcs and the direct current put into the magnet to produce the deflection of the arcs, then air is forced into the arc chamber where it comes into immediate contact with the flaming disc of arcs. There the nitrogen is partially oxidized by the high temperature. The gases then pass out through openings in the walls of the arc chamber.

To obtain the nitric acid in a useful form, the oxidized nitrogen and unchanged air pass to four nitric acid towers in series. Through a fifth circulates lime water which collects any nitric acid not absorbed by the water in the four previous towers. The water

in the latter partly charged with the acid is caused to pass through all the towers beginning at the fourth in the series. Strong acid is drawn from the first tower from time to time whenever it has attained the required strength, and is used as it comes from the tower or concentrated to suit the demand. At Notodden in Norway this process has been worked on a large scale since 1904 with a plant of 40,000 kilowatts capacity, and it is reported that a large increase will soon be undertaken. The very low cost of hydro-electric power in Norway no doubt makes it practical to work in a commercial way processes that would be successful in but few other countries. In this connection should be mentioned a new step in the nitrogen fixation field which is under development by the Badische Anilin und Soda Fabrik. Since 1907 a 2000 K.W. experimental plant has been in operation and a contemplated 120,000 H.P. installation is reported under consideration. In this process direct current is employed, whereby a distinct electric effect is said to take place, in addition to the thermal, producing a much more complete oxidation of the air passed through the furnace (reaching as high as 10 per cent. oxidized) and requiring a lower temperature to effect the change, thus lessening the liability of the nitric oxide to be broken up in its passage from the furnace to the cooling and collecting towers.

There was also established at Niagara Falls on a commercial scale a plant to produce a nitric acid by the electric arc, but so far it does not seem to have been a commercial success.

The processes for the production of nitrogen compounds by utilising the nitrogen in the atmosphere deserve particular attention, as they are destined to attain enormous proportions, and may be said to be converting the water-powers of the earth and the nitrogen of the air into indirect granaries for the food supply of the future.

Other arc processes of very considerable importance and magnitude are quite different in their application, those for the production of ferro-alloys and calcium carbide, for example. The description of the experimental test in the small electric furnace for the production of ferro-silicon will give a sufficiently clear idea of the working of a process for its manufacture, as well as that of ferro-chromium and other alloys, although, of course, a more modern type of furnace than the simple one described is now employed. This furnace is the series type single phase; the

smelting operations are carried on continuously and the metal tapped out at suitable intervals. Furnaces have been designed similar to this for 2000 to 3000 K.W. capacity, but those of one-half that size are possibly nearly as economical and more easily operated.

Before giving any description of the calcium carbide process, some explanation of the different furnaces which are in use will be interesting.

The Horry continuous ingot carbide furnace corresponds to a deeply flanged pulley with plates that bolt on and across from flange to flange, leaving a space in which the carbide is formed. This furnace is regulated by revolving the main circular body of the furnace away from the electrodes which causes the carbide to be formed in a circular ingot, the plates being bolted on at intervals on the furnace side, and taken off on the other so as to remove the carbide. The modern Willson furnaces for making carbide may be used either as ingot or tapping furnaces. When used for ingot they are fitted with trunnions so that the product can be dumped out when the pot is full, and cooled when the carbide is to be tapped; they are provided with a tap hole. In these furnaces the lime and carbon mixture forms the lining of the pot, and protects the iron work from the extreme heat. The operation of any of these furnaces is so very similar to that of the simple experimental one described earlier in the paper, that it will not be necessary to go further into each in detail. Many of the electric furnace plants are now equipped so that the current is automatically regulated, and the materials entering into the process for the production of the various products are usually handled wholly, or in part, by suitable mechanical means.

In the first furnaces for the production of calcium carbide, the arc was produced as set forth in the description of the experimental furnace, the pig being surrounded in the crucible by a body of the material from which the carbide is made. The early works were constructed and equipped to conform to this type, and, as far as

The lecturer distributed blue-prints illustrating furnaces that are actually in use for the manufacture of ferro-alloys, calcium carbide, etc. These include the Horry continuous ingot carbide furnace, the Willson furnaces for carbide, the Acheson incandescent furnace, the Hall electrolytic furnace, the Heroult electrolytic furnace and the Birkeland-Eyde oven. The noticeable simplicity of all the types of electric furnace is a very striking feature, and any designs which have been tested that change this feature were usually failures.

the production was concerned, were rather disappointing when large units were used and long runs made, as it was later found that the production per K.W. hour was low even at the best, for, as the length of the pig increased, the resistance of the carbide increased also. Carbide when cold is, for practical purposes, a non-conductor. It was necessary in the working of this furnace to pass a quantity of current through the pig of carbide in order to keep it liquid; and consequently the longer the pig, the greater the loss of energy, the production of marketable carbide falling as low as 6 lbs. per K.W. hour in plants operating this method, while in a more modern furnace design over 9 lbs. is possible under favorable conditions. This applies to an average quality giving approximately 4.75 cubic feet of gas per lb., and this is no doubt a very fair figure to give for the product on the market in the various countries now manufacturing or purchasing it, some going a little higher and others again less, but the present specifications call for a quality up to this standard.

Calcium carbide was one of the first of the electric furnace developments which gave great promise of becoming a very quick method of employing large units of hydro-electric energy. It therefore received a great deal of attention both in America and in Europe, and although Mr. Willson only discovered the process in May, 1892, by the end of 1894, or the early part of 1905, works were ready to start with a capacity of from 1000 H.P. up. From that time to the present its progress has been very rapid. The demand for the product for acetylene lighting purposes at times in the first few years exceeded the supply, and until extensions could be made there was a shortage. In some European countries where the patent laws are lax or non-existent, so many installations were put in for the manufacture of calcium carbide that in a short time some of them had to close down. To this fact the ferro-silicon industry no doubt owes much of its progress, as some carbide factories turned to this alloy as a profitable means of employing their surplus power.

In the production of calcium carbide, as well as in all electro-metallurgical processes generally, the raw materials are of the greatest importance, as the purity of the carbide is very much effected thereby; sulphur and phosphorus being particularly objectionable as they pass off with the acetylene. In the case of the phosphorus, it is dangerous, as explosions might be caused were

enough allowed to be present in the gas, and its presence makes purification necessary. All impurities are objectionable, as they lower the production per K.W. and lessen the value of the finished product.

The raw materials from which calcium carbide is produced are lime and carbon, usually coke or hard coal, all of which materials are crushed, the lime to about ½ inch mesh and smaller, the coke and coal to ¼ inch mesh and finer when ingot furnaces are used, and not so fine if tapping is practised. The lime and carbon are mixed thoroughly by mechanical means in the proportions of about 60 per cent. lime to 40 per cent. carbon, and, as in the experimental furnace, the arc is started and the material fed in as required. In the pot furnace, when the pot is full, an empty one is substituted, and the full one removed and allowed to cool, after which it is dumped and made ready to return to the furnace again, and so on. With the tapping furnace, carbide is tapped out when necessary, and the operation of the process carried on continuously. In the Horry furnace also the working is continuous, the circular pig being broken off from time to time and removed, while the process of producing carbide continues on the smelting side of the furnace. When tapping is practised, the molten carbide is allowed to run into a receptacle made of material sufficiently refractory to stand the hot carbide as it comes from the furnace without contaminating it in any way. The pig carbide requires some cleaning to remove the crust formed on the outside where the carbide is in contact with the unreduced material, which makes the temporary lining of the furnace, the last step being to crush it to the various sizes required and pack in 100 lb. steel drums.

The reaction taking place in the electric furnace for the smelting of calcium carbide is $CaO + 3C = CaC_2 + CO$. The various reactions which take place in the zone of fusion are simple, and no difficult problems arise as far as the actions of the materials are concerned. At the high temperature of the arc the calcium in the presence of the carbon vapor combines with the carbon forming calcium carbide, which remains in the furnace in a liquid bath until, in the Horry ingot furnace, the operation has continued long enough to remove portions of the ingot so far from the heat of the arc that it solidifies, when it can be removed, or as in the tapping furnace, tapped out at short intervals. There is some difficulty in

tapping carbide from the furnace, due to the fact of its being liquid at only a very high temperature, and in fact carbide of over 5 cubic feet per pound is not tapped in regular commercial operations (yet it is possible to produce 5.77).

The impurities in the carbide, such as unreduced lime and silica, lower its melting point, making it easier to tap. A very ingenious method of tapping is to apply an arc to the tap hole and melt away the chilled carbide until the flow is started, after which the flowing carbide keeps the tap hole clear until the furnace is sufficiently empty.

Another product of the arc division, which should really be classed with the calcium carbide industry, is that of calcium cyanamide, calcium carbide being the foundation of it. This is first manufactured in the regular way, after which it is pulverized, placed in a suitable furnace, and the finely pulverized mass raised to the necessary temperature of 800 to 1000 C, to start the union of the calcium carbide and the nitrogen, when union takes place according to the formula $CaC_2 + 2N$ $CaCN_2 + C$. The operation is assisted by the latent heat set free, and continues until the whole mass is converted. The nitrogen is allowed to enter into the furnace through a meter and suitable piping; this provides a means of knowing when the process is completed. Messrs. Frank and Caro found in their experiments that the presence of some compounds, calcium chloride, potassium chloride, calcium fluoride, etc., greatly promoted the union of the calcium carbide and the nitrogen by lowering the requisite temperature by about 200 degrees centigrade.

A source of nitrogen is the Linde process; air is first liquified and allowed to evaporate. Since the nitrogen distils off at 13 C. lower temperature than the oxygen, this is allowed to boil away by raising the temperature or reducing the pressure, leaving the oxygen behind. The copper process consists in passing air over hot copper particles which unite with the oxygen but allow the nitrogen to pass on.

The marketable product, which is called nitrolime or lime nitrogen, in its crude form, contains about 57½ per cent. of pure calcium cyanamide, or the equivalent of 20 to 22 per cent. of nitrogen, approximately the same as ammonium sulphate, which is theoretically 21 per cent. This nitrolime contains also calcium oxide, silica, iron oxide, alumina and some carbon which gives it the blackish color.

It is estimated by Dr. Frank that 2½ H.P. is necessary for fixing one ton of nitrogen, and ¼ H.P. for grinding, etc. This added to what is required to produce the carbide would necessitate, if it were proposed to substitute nitrolime for sodium nitrate, the erection of plants to the extent of 800,000 H.P. This state of affairs in the field of nitrogen products is almost within sight, and plants are being erected in Europe totalling thousands of H.P. for the manufacture of calcium cyanamide. At Niagara Falls there is a large plant in progress for this purpose at the present time. The product is to be used for fertilizing and for the production of ammonium compounds.

The electrolytic division which is the next to be considered is also next in importance. The three greatest uses of this branch of electro-metallurgical processes are the production of aluminium, the electrolytic purification of copper and the production of caustic soda and bleaching powder; the first is an electrolytic smelting operation; the second corresponds to electro-plating and is carried on in an acid bath the temperature of which is below the boiling point of water; the third is similar to the second, the salt is dissolved in water and then acted on, the caustic soda collecting at one pole and the chlorine being recovered at the other and taken up in freshly slacked lime forming chloride of lime, "Bleaching Powder."

Sir Humphrey Davy in 1809 was undoubtedly the first to obtain metallic aluminium, but was not successful in isolating it from the iron in which it was collected. In 1827 Friedrich Wöhler first produced aluminium in its metallic form, but not until 1854 was it isolated in practically a pure state by Sainte-Claire Deville who determined its true properties. From that time until about 1888 practically nothing of importance in the production of aluminium was done, although some small quantities were produced in chemical processes in connection with the sodium industry. In 1886 Hall applied for a patent which was granted in 1887, and works were erected in 1888. About the same time Dr. Heroult of Paris applied for a patent in the U.S.A., but was antedated by Hall by two months, although both were working, no doubt, independently.

This process is carried on in a carbon-lined pot which forms the cathode or negative pole, while the carbons, about 3 inches in diameter by 18 inches in length, form the anode or positive pole.

The current is delivered to the pots at 160 volts, and a drop of something over 5 volts occurs in each pot with a consumption of electric energy equal to about 65 H.P. A sufficient number of pots are put in series to absorb the 160 volts. In this process about 2.9 volts is required in the chemical work of decomposing Al_2O_3, and the remainder consumed in keeping the bath at the necessary temperature (850-900 C.) to maintain its fluidity. The current efficiency can be reckoned at over 85 per cent.

In operating this process the "Hall" bath is made; it consists of cryolite to which is added aluminium fluoride and then alumina. The alumina dissolves in the bath. In the reaction oxygen is set free when the Al_2O_3 is broken up by the current, and combines with the carbon of the electrode forming carbon monoxide, the aluminium being deposited on the bottom of the pot which acts as cathode, and is tapped out as pure metal when required, the purity being 99 to 99½ per cent. for the high grade, the second grade running possibly 97 to 98 per cent., the impurities being 0.1 per cent. iron, 0.3 per cent. silicon in the first grade. The yield of metal per K.W. year will approximate 600 lbs.

The alumina, the source of aluminium, is obtained principally from bauxite found in the southern part of U.S.A. and elsewhere, some large deposits being in Georgia. This bauxite has to be freed from iron oxide, silica, etc. This purification of the bauxite is one of the chief expenses in the production of the metal, possibly making the cost of the alumina equal nearly to one-third of the total.

There have been some attempts to produce the metal more directly from the bauxite by using the electric furnace for purifying the alumina, the result aimed at being to reduce the foreign oxides to the metallic state leaving the alumina unreduced; the alloy of the metals, making up the impurities, collecting at the bottom, due to their greater specific gravity, but so far it does not seem to have succeeded.

The incandescent or third division will be best understood from the work as carried out in the production of "Carborundum" (the trade name for carbide of silicon), and graphite; but there are other uses to which is applied the incandescent principle, as, for instance, to some of the iron processes. In the manufacture of carborundum, which was discovered commercially in 1891 by Acheson, and a commercial plant erected at Niagara in 1894, the

Acheson furnace is employed. This furnace is operated intermittently; the charge consists of a carbon core, surrounded by a body of the mixture which is made up of sand and carbon in the form of coke and salt, the formula being $SiO_2 + 3C = SiC + 2CO$. This process is commenced by using a current of possibly 200 volts or more to heat the core and thus decrease its resistance, after which the voltage is lowered gradually by suitable electrical apparatus, and the current is gradually increased and kept up until the surrounding charge is converted into carbide of silicon, "carborundum." The charge is then left to cool, after which it is separated from the surrounding unconverted material. The furnace charge consists of approximately $\frac{1}{2}$ ton carbon core, the carbon in the mixture representing about $3\frac{1}{2}$ tons, to which is added about 6 tons sand and $1\frac{1}{2}$ tons salt. The result of a 36 hour run using say 1000 H.P. will show from 3 to 4 tons of carborundum in the form of crystals. When removed from the furnace it is ready for use as an abrasive, suitable grading, moulding, etc., being all that is necessary before marketing. The furnace is a very simple one; it is 8 to 10 feet long, and the electrodes enter through the brickwork ends, the sides being bricked up each time as the charge is put in, and removed when being emptied. About 1000 H.P. is a fair sized furnace.

The process for the artificial production of flake graphite and graphitized carbon for electrodes and other uses grew out of the carborundum industry. Part of the surrounding carbon was found to be converted into graphite, as also part of the core, and this gave sufficient promise to justify the establishing of furnaces for this purpose. Later a large plant was erected to produce flake graphite, graphitized electrodes, etc. For graphitizing amorphous carbon in different shapes, a furnace similar to the Acheson carborundum furnace is used; the pieces are packed crosswise in the furnace and filled in between with material of lower conductivity, to cause an increased resistance in the furnace, enabling high voltage to be used, and therefore, much larger and more economical operation and construction. It has been contended on good authority that the change takes place entirely by reason of the high temperature to which the amorphous carbon is subjected, but it now appears that the change is much more rapid when other substances are present, such as metallic vapor of iron, which are supposed to assist in graphitization.

The production of "graphitized electrodes" for electric smelting work has had a far-reaching and beneficial effect on the kindred electro-chemical industries, removing, as it has, many of the troubles arising out of the low conductivity and liability of cracking in the amorphous carbon electrode previously used, as well as allowing a much higher current density in the electrode and also in the furnace when desired; besides on account of their softness it is possible to machine them readily for any connection required. It is practicable, also, to produce a very high grade of flake graphite by the electric process, all of which products makes this branch an important one.

The iron and steel electric smelting possibilities which might be classed in the first and last divisions, or both, is a subject well worthy of separate treatment, and a great deal of time might be profitably devoted to it, as its possibilities are not yet understood or appreciated. Steel is now being produced in America by the electric furnace, and at Heroult, California, an experimental iron furnace is in operation, but not much practical progress has been made, particularly in America, along the lines of direct production of steel from ore.

These brief descriptions and observations on electro-metallurgical processes in a general way will give some idea of the practice at the present time, but the many products which are now made and those which are almost daily added to the list, make it impossible in a short paper to touch on anything except those processes necessary in explaining the principles involved. It is a growing industry pushing itself into almost every branch of metallurgical activity, and it is doubtful if even the most enthusiastic have got a glimpse of its ultimate development, which will transform the waterfalls of this continent into useful agents helping to do man's work, and to some extent compensate for the reckless waste of natural resources whose abundance has led the present generation, of America at least, to consider almost inexhaustible.

To those who are devoting their energies to the development of electro-metallurgical processes of any kind, as well as to the citizens of every civilized country, the preservation and economic development of all natural water powers should be of the greatest importance, and should receive their aid and protection to the

utmost, as this is a source of energy, which if properly safeguarded will be indestructible and inexhaustible. Without this power electro-metallurgical processes cannot be economically carried on.

WOOL CULTURE.

By Jas. P. Murray.

Wool growing and the manufacture of woollen fabrics are subjects of interest to the farmer and to the manufacturer alike. While the latter is concerned with those properties of wool which render it valuable, the regulation of the quality lies largely in the hands of the former.

From the manufacturer's standpoint, wools may be divided into two classes: those of long staple suitable for combing into worsted yarns, and those of short staple suitable for carding into woollen yarns; each particular class of yarn being characteristic of the fabric produced therefrom. In general the manufacturer seeks to secure fleeces, the fibres of which are: uniform, sound, supple, elastic, lustrous, soft to the touch, of good colour, well nourished, evenly distributed over the whole surface of the carcass, and as nearly equal in length as possible over the longest portion of the fleece.

To obtain these results great care in the selection of the breed should be exercised, while the climate and the nature of the soil must also be considered as these also affect the quality of the wool. For instance, sheep fed upon herbage grown in a chalky district produce wool with a tendency to coarseness, whereas the same sheep will yield fine and silky wool if reared upon a rich, loamy soil. Fortunately for the farmer there is an almost unlimited choice of breeds, for no domestic animal responds more quickly to its environment than does the sheep. To Robert Bakewell belongs the honour of pointing out, in the latter part of the eighteenth century, the biological principle that the characteristics of the parents are transmitted to their offspring until fixity of type is attained. To the study of this fertile principle may be attributed the excellence of modern flocks.

The manufacturer, concerned only with the wool, is interested in certain qualities which it possesses such as, for example, the uniformity, which means that in the ideal condition, one fleece would be a fair sample of a flock.

To satisfy the buyer then, the farmer must strive continually to keep up the standard of his flocks by careful selection and the

maintenance of the health of the animal. For the proper nourishment of the fibre on which the value of the wool depends, a proper use of preparations for the destruction of parasites in the skin is necessary. The old-time " smears " which have an injurious action on the skin and wool, should be replaced by the modern arsenical dips; these, which contain also alkalies and sulphur in a soluble form, are not only germicidal but are very easily removed from the fibre during washing. The skin is thus kept clean and healthy and the most favorable conditions are provided for the growth of the wool.

The washing of the sheep is likewise important, and unless this can be done in running water it is better left to the wool comber, in any case the " suint " to which the wool owes its elasticity and life must not be removed. The object of washing is to remove the dirt only, which affects very considerably the commercial value.

The wool buyer is of as much importance to the farmer as the wheat buyer or the fruit merchant, and on the other hand the farmer is also important from the buyer's standpoint. Their mutual interest should therefore lead to reasonable consideration of each other's position, and tend towards a constant improvement in quality.

From the farmer's point of view the importance of sheep and wool culture cannot be too greatly emphasized. If he looks at it from a business standpoint, all the ills under which sheep growing is supposed to suffer will disappear, and while it is to the advantage of the manufacturer to support the efforts of the farmer, he cannot be responsible for the proper promotion of the latter's business.

If the farmer continues to treat his wool as a by-product worth but little care, the buyer will soon look elsewhere and pay 10 to 20 higher prices for a good article. The requirements for the treatment of wool as drawn from the best experience are not very exacting and may be summarized as follows.

(1) Do not let the sheep run too long after washing before clipping, or all the advantages of the wash will be lost.

(2) Do not clip the wool wet as it tends to promote rot or mildew.

(3) Be most particular that the clipping is done in a scrupulously clean place, free from dirt, chaff, straw, binder-twine or any other matter foreign to wool by which it may become contaminated.

(4) Remove all dung, locks, cots, tailings, skin wool, etc., and tie the fleece up with woollen bands made from the fleece itself, instead of using string, twine or even straw, as any traces of these materials are sure to show up afterwards in the manufactured fabric after dyeing, resulting in much damage and loss of time for their removal.

The aim of the manufacturer is to retain those natural peculiarities of the fibre which the farmer has striven so zealously to develop. Unfortunately, however, all manufacturers do not seek virgin wool as their raw material, and in Canada to-day there is to be found in the clothing on the market such materials as: "shoddy," "mungo," "flock," "kuntzwolle," "laine renaissance," etc. These were once the original product of the sheep but have been used over and over again until all the resilience is exhausted, and only the skeleton of the fibres is left. This is mixed with new or virgin wool, and with some yarns of all new wool, is made into fabric, then into clothing and sold to an innocent public as " all wool." This class of merchandise is difficult to judge and causes much trouble to the customs appraiser. To prevent the manufacture of such fabrics from dirty rags and like material, it is evident that the growing of wool must be stimulated. This can probably be best effected by the establishment of assembling sheds to which the wool grower may send his clip. Each batch of wool should be weighed, examined, sorted and standardized by qualified wool experts, and a penalty of some kind imposed for dirt exceeding a certain percentage. The grower should be able to get a warehouse receipt which would be negotiable, and there should be proper baling facilities with a business method of shipping. Samples should be submitted at the world's markets and the commercial value established. Freight rates should be adjusted to meet necessities, and manufacturers should be encouraged by measures which will warrant the investment of capital and the employment of labor.

Organization among the wool growers will be the first step forward, and in this direction there are excellent examples. The apple growers of the western states, the melon growers of the middle

states and the peach growers of our own Niagara Peninsula are all organizing and planning for the improvement of the grade of the fruit, for better conditions in packing, shipping, marketing, and for more favorable freight rates and insurance. The results of this policy are that the consumer is obtaining better fruit earlier in the season and at less cost, while the grower is earning a reasonable return on his investment.

Such a policy is urged on the wool growers who might organize an association and improve the condition of the industry by similar lines of endeavor. A movement of this kind would be of advantage to both the grower and the manufacturer, and would materially hasten the progress of Canadian industry.

There are many problems for the chemist in the growing and manufacturing of wool. Apart from the cleaning and dyeing in the factory, the questions of fertilizers and fodders fall within his province. To him the farmer must look for advice in the treatment of the soil and the choice of a suitable fertilizer from among the many which are offered in the market to-day. The study of the food values of various fodders is also a chemical problem and the utilization of new materials for this purpose must be constantly kept in mind by the chemist who devotes his attention to the subject.

In the factory, there are still the problems of the recovery of values from the scouring liquids and the utilization of the refuse from the dust willow, which await solution. Only recently in Toronto, this latter product has been used as a fertilizer with excellent results which may serve as an instance of the useful employment of a waste product.

Technical education is a prominent question to-day, and it is to be hoped that an interest will be aroused in a set of industries so natural, indigenous, essential and interdependent as wool culture and wool manufacture. The country which encourages its manufacturers is bound to build up a large and prosperous industrial population to which the farmer can look for an ever-increasing market.

THE USES OF THE RARE EARTHS.

By Prof. Charles Baskerville, Ph.D., F.C.S.,

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The so-called " rare earths " constitute almost a quarter of the number of known chemical elements. Many of the names found under this head refer to chemical compounds, whose definiteness of character has not been sufficiently determined to warrant their being given a place among the elements.

These earths have been classified under three groups: (1) The *cerite* earths, including cerium, lanthanum, praseodymium, neodymium (together with didymium), samarium, gadolinium and europium; (2) the *yttrite earths*, including yttrium, erbium, terbium, ytterbium, scandium, holmium and thulium; (3) the *zirconium group*, including zirconium, thorium and germanium. The classification is based on the following chemical facts: All of these earths are precipitated from acid solutions by oxalic acid. The elements of group 3 are separated from the other two groups by precipitation with sodium thiosulphate. The other two in solution are separated from each other by treatment with sodium or potassium sulphate, which precipitates the double sulphates of the cerite group, while the yttrium earths remain in solution.

The methods of extraction are somewhat complicated, hence I do not feel that it would be quite considerate to rehearse those found in certain works on the subject, and professional obligations prevent my speaking of others not published.

Reagents. Investigators in the rare-earth field have been most anxious to secure more satisfactory reagents to be used, not only for the detection, but also for the separation of this " nebula of elemental matter," as Crookes once named the yttria earths. A recounting of the numerous researches along these lines is beyond the scope of this address. A limited number of reactions have been observed with cerium which are of a contrariwise service. The result is, cerium and its compounds now serve to a degree as reagents in analytical chemistry; as such they have a value, like arsenic, osmic, molybdic and tungstic acids. The other rare earths so far have given results which exclude their consideration in this respect.

Sonnenschein, whose announcements were verified by Djuberg, found cerium dioxide to be an excellent reagent for the qualitative detection of strychnine and other alkaloids. A solution of a minute quantity of cerium dioxide in concentrated sulphuric acid is colored intensely blue by the slightest particle of strychnine. Other colors are produced by other alkaloids. According to Pflugge the reverse of this reaction is an excellent test for cerium.

Boussingault suggested that cerium phosphate, which is insolul in nitric acid, be used for the quantitative separation of phosphorus in iron and steel. The method has not been applied practically with success.

Sonnenschien also recommended the substitution of ceric solutions for potassium permanganate in volumetric analysis. In this connection, Job says that the strong oxidizing action of these solutions is more effective in certain cases than the permanganate.

Recently Foerster called attention to the use of cerium sulphate as a technical oxidizing agent for chemical preparations. Meister, Lucius and Brüning have patented the use of cerium compounds as oxidizing agents for aromatic hydrocarbons. By means of the dioxide, toluene has been converted into benzaldehyde. Anthracene, by means of ceric sulphate, is converted into anthraquinone; naphthalene, into naphthoquinone and phthalic acid. Muthman and Most used cerium salts for electrolytic oxidation in preparing organic compounds.

At present, the pages of the purely scientific chemical journals contain more contributions to our knowledge of these rare earths than at any time in the history of chemistry. This promises the knowledge which brings utility.

Photography. Lumiére and Seyewitz found ceric sulphate an excellent oxidizing agent in reducing photographic reproductions. When acidified with sulphuric acid, ceric sulphate keeps indefinitely, and acts uniformly upon the plate without causing striæ or fogging.

The Lumiére Brothers proposed another application of the cerium salts to the photographic art, based on their sensitiveness to light. Thus, if a paper, wet with cerium nitrate or cerium sulphate, be exposed to light, a reduction from ceric salts to cerous salts takes place on the illuminated portions of the paper.

If this copy be developed with certain substances of the aromatic group (viz., phenol, amido-benzoic acid, etc.), vividly colored pictures are obtained. However, these applications have not been put into effect to any extent.

Therapeutics. Attention was attracted comparatively early to the physiological properties of cerium salts and their applicability for medical purposes. Thus the eminent gynecologist, Simpson, in the early seventies of the last century, recommended cerium oxalate as an efficacious remedy for *Vomitus gravidarium*. Although in succeeding years opinions differed widely as to the value of this preparation, it was nevertheless incorporated into the pharmacopœias of various countries. *Cerium oxalicum medicinale* contains besides cerium, considerable quantities of other rare elements. Subsequently the therapeutic application of cerium oxalate was extended to the treatment of sea-sickness, epilepsy, headache, etc. Several other cerium salts were introduced for medical purposes together with the oxalate. Thus Mackay recommends the use of cerium-ammonium citrate. Cerium hypophosphite is said to be applicable to phthisis.

According to the researches of Wasilieg and Bokorny, the cerium salts possess poisonous properties. Drossbach, who conducted similar experiments on the salts of other rare elements, observed the bactericidal effect of such preparations. A practical process mentioned by the latter, for the preservation and disinfection of decaying substances, calls attention to the use of diluted solutions of lanthanum, yttrium, erbium, and ytterbium salts.

According to later investigations conducted by J. Schmidt, the use of *didymium chloridum*, $DiCl_3(H_2O)_6$, as an antiseptic in veterinary medicine gave unsatisfactory results. Among the various rare earth antiseptics that have been suggested, may be mentioned the nitrates of cerium, lanthanum, "didymium," the compound salts of cerium with bismuth, cerium oxalate and salicylate (as a sprinkling disinfectant), and the disulphates.

Rare-earth preparations have not been sufficiently tried in medicine to warrant their adoption as yet. Systematic investigations on the physiological action of these substances, assisted by the writer, were carried out in the laboratories of the Medical College of Cornell University and of the College of Physicians and Surgeons of Columbia University. It was demonstrated that these bodies possess no characteristic therapeutic value.

An American patent was recently granted Armand Müller-Jacobs for the use of zirconium nitrate for the preservation of food, etc. "The substance is immersed in a suitable concentrated solution of a zirconium compound capable of emanating radio-active rays." As zirconium compounds emit no radio-active rays nor give off an emanation that has been recognized as yet, the preservative action is doubtless due to something else, if there is any.

Pigments. The oxides of certain of the rare earths are characterized by colors, hence repeated proposals have been made for their use as pigments. For instance Strohecker suggested the use of the cerium oxides (obtained by him from the Hamstädt cerite clays) for painting purposes. According to Müller, the cerium colors of Strohecker proved to be mixtures of iron oxide, lime, clay, etc. A process for making rust-proof colors by means of peroxides of cerium earths is due to Kosmann. According to the patent, the peroxides of the cerium earths must be ground, singly or in mixtures, with linseed-oil varnish, with the addition of a siccative. The register of patents also contains a process of the Rummelsberg chemical factory, of Berlin, for the production of colors from rare earths. According to this process, the dark-brown powder obtained from the glowing of praseodymium salts of volatile acids (praseodymium peroxide, Pr_4O_7) yields an earth color of excellent covering and durability.

The application of pure praseodymium compounds as pigments is now out of the question on account of the expense. It is possible that mixtures of the oxides, which are readily obtained as by-products in the treatment of various minerals, monazite, for example, may be used. It remains to be determined, however, whether these bodies possess sufficiently unique and durable tints to warrant the cost. The colors of the mixed oxides vary from a cream to a reddish brown and even black (0.5 to 1 of praseodymium peroxide for the latter two), according to the presence and amount of praseodymium.

Dyeing.—A number of propositions have been made looking to the application of the peroxides of the rare metals in the textile industry. In 1898, a process was submitted to the Société Industrielle de Mulhouse in a prize essay. According to Kosmann, colors are produced by simply boiling the web with solutions of cerium salts, and then treating it with an ammoniacal

hydrogen peroxide solution. Thus yellow and orange are produced from cerium, straw-yellow from lanthanum (impure) and "didymium" salts, and some doubtful brown colorations also. Kosmann also describes in this essay some special methods for the modification of the colors obtained by means of salts of the heavy metals, tannic acid, etc. According to the experiments of Brylinske, and of Wagner and Müller, the yellow shade produced by oxidized cerium compounds is of poor appearance, and deficient in fastness from soaping.

Barnes, in extending his work on the use of titanium oxide as a mordant for wool, noted that zirconium oxide with alizarin produced a color very much like one produced by chromium. According to him, cerium does not appear capable of yielding a mordant for wool. When wool is boiled in a solution of a cerium salt it does not take on any color in the dye-bath. He produced colors on cotton with a cerium mordant, but they were quite worthless, being readily destroyed by weak acids.

Mordants. —Otto Witt gave the first detailed directions for the use of the rare earths as mordants. His researches were confined to the use of cerium sodium nitrate. The color was developed by steam. The cerium mordants were also investigated by Matschak and Scheurer; Brylinske, also, studied yttrium salts. Gandourine considered the sulphates of "yttrium, lanthanum, erbium, cerium and didymium."

Kruis, Böttger and Bühring have maintained that cerium disulphate is an excellent developer of aniline black. Witt, on the contrary, states that the double nitrate of cerium has no effect on the production of aniline blacks. He attributed the effect to impurities, possibly vanadium. According to him, the colors produced on the material, mordanted and passed through boiling soda solution, are tolerably fast to soap. The shades given were intermediate between those given by chromium and iron mordants.

The speaker, with assistants, used the sulphates, acetates, and hydroxides of lanthanum, neodymium, and praseodymium. Although there was a mordanting, the colors "produced were not of a bright shade, and not always very fast to washing. The rare earths can have little practical application as mordants for the following reasons: (1) because they do not possess the mordanting action to a degree which would allow competition with known mordants; (2) because the supply is somewhat limited, and would

not admit of extended use; (3) their cost, which, even in the event of the first and second considerations being favorable, would bar their practical use extensively."

Glass Coloring. Schott and Glinzer, in Jena, succeeded in introducing oxides of cerium, "didymium," and erbium into molten glass, in quantities of over 10 per cent. Zsigmondy examined, with reference to thermal conductivity, a glass in which the calcium oxide was partly replaced by cerium and "didymium" oxides. Its thermal conductivity equaled that of lime glass. Witt obtained yellow-colored glass, resistant to heat, by additions of 1 to 3 per cent. of cerium oxide. "Didymium," neodymium, and erbium oxides color molten glass red to violet; praseodymium, from yellow to yellowish green. The glasses gain no practical value through this coloring, but they offer a certain scientific interest, inasmuch as they afford a convenient means for observing the absorption spectra of the respective earths which enter into their composition.

On the coloring properties of the oxides of neodymium and erbium is based a process, by Drossbach, for decolorizing glass. If we add to the molten glass a salt of neodymium or erbium, the rose-red coloration produced by these ingredients removes from the glass its usual bluish-green tint.

Fireproofing. Nernst has recently indicated a possibility of applying a number of the rare earths for the production of fireproof utensils and vessels. It is quite apparent that this is a useless suggestion on account of cost.

Catalytics. Imray secured an English patent for the use of oxygen compounds of the rare earths as a contact material, with or without the addition of platinum, for the production of sulphur trioxide. Baskerville and Davis independently discovered this also. The best process so far made known appears to be that of Hölbling and Ditz, who make use of the residue resulting from the manufacture of thorium salts, as a contact substance for the production of sulphuric acid and its anhydrides. A certain definite proportion of didymium sulphates is required, according to later reports, for securing a maximum yield. For some reason, however, they have been unable to secure U.S. patents.

Ditz and Margosches pass hydrochloric acid gas over a heated contact-mass consisting of a number of chlorides of the rare earths. Under favorable conditions (at a temperature of from

350 to 450 C.), about 75 to 90 per cent. of the hydrochloric acid is said to be decomposed with the liberation of chlorine. Modern electrolytic processes for the production of chlorine make this useless.

Electric Batteries. Several of these rare-earths, especially those of the cerite group, form a variety of oxides, as CeO, CeO_2, Ce_2O_3, Pr_2O_3, Pr_4O_7, PrO_2, etc. The construction of a storage battery, devised by Welsbach, depends upon the electromotive behavior of the cerium oxides. The electromotive force of a reversible battery (consisting of zinc amalgam, zinc sulphate, cerous-ceric sulphate, carbon) is said to exceed that of the lead accumulator, although it is doubtful if this cell can compete with the lead cell in its results. The cerium-zinc-sulphate electrolyte, which may be regenerated, can be used advantageously as a substitute for the chromic acid solution in the immersion battery. According to Bauer and Glaessner, there is no hope of practically producing cells from aqueous solutions of cerium salts. This does not, however, preclude the use of cerium oxides as catalyzers in cells with fused electrolytes. If the public press accounts of the Edison cells are correct, this can have no value.

General. In recent years Muthman and his co-workers have investigated exhaustively the utilization of the metals of the rare earths. The metals were obtained by electrolyzing fused chlorides in copper crucibles, water-jacketed, with carbon electrodes. The cerium thus obtained gives brilliant sparks when scratched with steel. The pyrophoric bodies thus produced, as well as those alloys of Welsbach, which possess a similar property, have so far not been put to any extensive use that is well known. However, Escales has secured a patent for the production of lighting masses, based upon the reduction by means of magnesium and aluminium. He, also, patented a process for obtaining metalloids or alloys of the rare earths, which are said to possess even greater reducing powers than aluminium itself.

Siemens and Halske secured patents for the production of electrically incandescent bodies from the rare earths. Sander produced on conductors of the second class metallic films or crusts. This was accomplished by the reduction of the oxides or other compounds of the rare earths by means of potassium, sodium, or magnesium in a vacuum, or in the atmosphere of an indifferent gas.
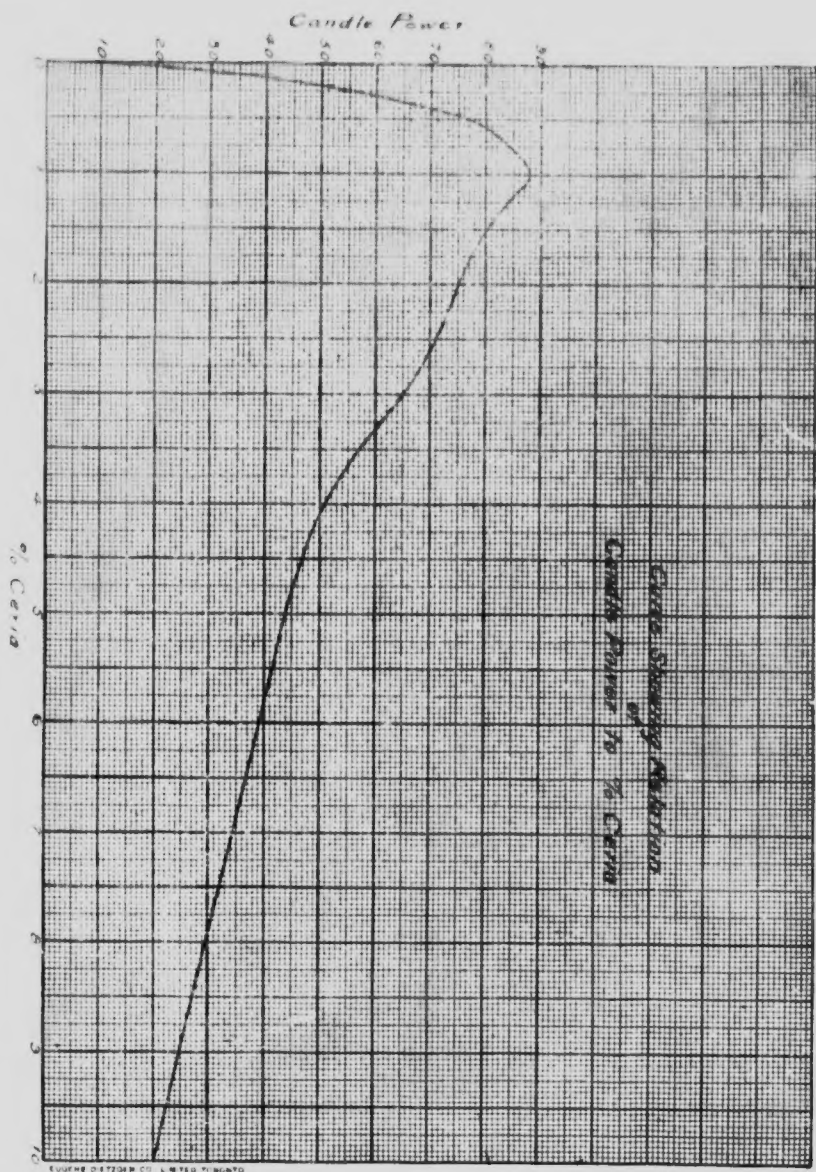
Illumination. As early as 1826, Drummond evolved the lime-light. (It is claimed by some that Guerney (Sir Goldsworthy) dis-covered the lime-light (1793-1875)), which depends upon directing an oxy-hydrogen flame on a pencil of calcium oxide. Tessie du Motay, in 1867, substituted bituminous coal gas for the hydrogen. Lime was found not to answer the full requirements, on account of slaking when not in use, so Linnemann substituted a plate of zircon-ium oxide. Koch also prepared, for medical purposes, porous glow-pieces of zirconium. Klotinsky used various oxides, among them zirconia, and gaseous or pulverized hydrocarbons, whose combustion was facilitated by oxygen. Clamond suspended his glowing material in the form of a basket over a central spiral tube, from which issued a mixture of the gas and heated air. Fahnehjelm formed the incandescent portion out of fine, flat or round, needles, set close together and suspended in a rack above the burning mixture; water-gas was used. While this was reported as successful in Germany, in the three places it was tried in America (Chicago, Jackson, Mich., and St. Joseph, Mo.), it was found impracticable.

Haitinger prepared a mantle for incandescent gas-lighting, composed of aluminium and chromium oxides. It gave a rose-red light, but did not possess the necessary resistance to atmospheric influences and mechanical shock. In 1885, Carl Auer obtained his first patent for a mantle to be used in incandescent gas-lighting.

At first, thorite and orangite were the sources of the thoria. The location of the somewhat extensive deposits of monazite, a double complex phosphate and silicate of the rare-earths, sands in the Carolinas and Brazil gave larger sources of raw material.*

It will be of interest to note the lowering in price of thorium nitrate due to its increased use, to new sources of the raw material, to improvements in extraction, etc. Prior to 1893, the price per kilogram varied between $125 and $500. Now it may be had for from $7 to $10 per kilogram. (Prices went off some-what with the attack of the Austrian Welsbach Company on the "Thorium Convention" in December, 1909, but it would appear that there is some possibility of an understanding).

* The speaker then described, using lantern slides, the manufacture of the Welsbach mantle, and showed the difference in quality and quantity of light produced by varying the percentage of cerium oxide.

Candle Power

% Cerra

Curve Showing Relation
of
Candle Power to % Cerra

EUGENE DIETZGEN CO. LIMITED TORONTO

Many attempts at devising other incandescing mixtures have been made. As a consequence, there have been many patents taken out, the number touching the mechanical side of the problem being great. Drossbach experimented with mixtures of the heavy metals and alkaline earths.

Nernst learned that certain substances which are non-conductors (practically) of electricity when cold, become conductors when heated to a high temperature. He made a cylinder of magnesia provided with electrical connections. This was heated by a Bunsen burner to make it a conductor. The passage of the current then rendered it incandescent.

Beebe, who formerly was chemist to the Nernst Lamp Co., Pittsburgh, has published a full account of the methods of treatment of the ores for the extraction of the rare oxides used. There is also an excellent discussion of some of the principles involved in the making of the glowers. The lamps are excellent in many ways, but up to the present there are certain physico-chemical difficulties which shorten their life.

Wedding, in Germany, has prepared a zirconium lamp, by submitting the zirconium oxide with magnesium to the action of hydrogen at high temperatures. The alloy obtained is pulverized, and, on the addition of a cellulose solution, it is transformed into a plastic homogeneous mass from which the filaments are drawn. The filaments, after being carbonized in an atmosphere free from oxygen, present a metallic appearance. One pound will furnish fifty thousand filaments. The zirconium filament is reported to consume a current of two watts per candle-power, and to run with a current of 37 volts. Three of the lamps can be conveniently placed in series across the usual 110 volt circuit. The lamp has a life of from 700 to 1,000 hours. Wedekind states that these filaments in reality consist of a mixture of compounds of zirconium with nitrogen, hydrogen, and carbon, to which rhodium is also added to obtain the necessary conductivity.

Adel made filaments for incandescent lamps from vanadium, thorium, columbium, and their alloys, by subjecting them in the form of amorphous bodies, without a binding material, to a pressure sufficient to make them of the desired shape.

The history of many industrial applications of the principles of science has not seldom shown the development of a branch to a

greater extent than the parent stem. So far this has not proved to be the case with the rare earths found with thorium and zirconium, although tons of these by-products have accumulated.* They await the discovery of a commercial demand. The prices at which these rare materials are quoted in chemical catalogues and trade journals are purely provisional and the values are fictitious, and need not deter one inclined to exercise his ingenuity along these lines. When the demand is created, it will be met as in the case of thorium. That many have already busied themselves with the problem appears from what has been said. But so far little has really been accomplished with these by-products. The real object of my lecture has been to call attention to this. If I may have stimulated some one to take up the problem and cause him to secure results, I shall feel my work as a teacher has been well done. The teacher may not be the torch bearer, but he may kindle the torch of him who holds it aloft that the world may see.

* It takes about 100 g. of the purified monazite sand to yield enough thoria for an average mantle. About 40 million mantles was the output of the United States manufacturers last year. This required 4000 tons of monazite. The by-product amoun   about 35 per cent.